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METALLURGICAL ANALYSIS

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METALLURGICAL ANALYSIS

BY

NATHANIEL WRIGHT LORD, E. M.

Late Professor of Metallurgy and Mineralogy, Ohio State University

AND

DANA J. DEMOREST, B. Sc. in Chem. Eng.

Professor of Metallurgy, Ohio State University

Fourth Edition

Revised, Enlarged and Reset

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PREFACE TO THE FOURTH EDITION

The fourth edition of this book contains about ten pages more than the third edition. This additional matter consists largely of amplification of methods presented in the previous edition.

At the same time advantage was taken of the opportunity to correct errors discovered in the third edition, to eliminate some ambiguities of expression and make changes in the arrangement, with a view to securing a greater degree of uniformity in the presentation of the methods.

D. J. DEMOREST.

February, 1916.

PREFACE TO THE THIRD EDITION

In preparing this edition of "Metallurgical Analysis" the writer has retained as closely as possible Professor Lord's method of presentation of the subject.

The book has been rewritten so as to incorporate in the old methods the recent advances in knowledge bearing on them. Also many new subjects have been added so as to include in the book practically all the methods of chemical analysis likely to be used by the metallurgical chemist.

The chemical factors have all been calculated from the international atomic weights for 1913.

The writer wishes to acknowledge his indebtedness to Prof. E. E. Somermeier for his encouragement and help.

D. J. DEMOREST.

August, 1913.

PREFACE TO THE SECOND EDITION

In preparing the present edition of this book the writer has endeavored to extend its scope and make it not only a text-book for students in technical schools, but also a book of reference for young men in metallurgical laboratories. With this object the book has been enlarged so as to include methods for the determination of all the elements likely to be encountered in the ordinary work of the laboratory. The subjects of gas analysis and the testing of fuel have been treated at much greater length. To the standard processes given in the first edition such recent ones have been added as have proved to be of general application and value. The descriptions of the processes have been largely rewritten and the notes extended and as far as possible brought up to the present state of the science.

To the descriptions of special forms of apparatus cuts have been added. These generally show simple arrangements which have been found by the writer to be well adapted to the use of students and not to require expensive material.

The writer wishes to acknowledge his great obligation to his associates, Professors Wm. McPherson and W. E. Henderson, for their assistance in the reading of the proof and for valuable suggestions, and especially to Mr. E. E. Somermeier, Instructor in Metallurgy, to whom he is indebted not only for assistance in revising the manuscript and reading the proof, but also for working up in the laboratory many of the details in the descriptions of the processes.

January 31, 1903.

PREFACE TO THE FIRST EDITION

These notes were written for the use of the writer's students in the metallurgical laboratory of the Ohio State University.

The object was to give in a condensed form the series of selected methods in metallurgical analysis which made up the course of study.

To the descriptions of the processes, such explanations have been added as experience has shown to be desirable for the assistance of the student in understanding the conditions necessary for accurate results.

Such methods only are given as have been tested by repeated use in the laboratory and found satisfactory.

No attempt is made to describe general reagents or apparatus, as students prepared to take this course are always familiar with all ordinary laboratory equipment, and for special forms of apparatus reference is made to easily accessible books and papers.

The writer wishes to acknowledge his obligation to Blair, Troilius and other standard writers, as well as to numerous papers in the various technical and scientific journals, though it has been impossible to give credit in detail to all the sources from which material was taken in compiling these notes.

The references added are only those which it seemed important the student should consult for fuller information on the subject.

October 28, 1893.

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INTRODUCTION

Before beginning the course in special analysis given in these notes, the student is supposed to be familiar with the ordinary qualitative reactions of the acids and bases, the preparation of reagents, and so much of the general methods of quantitative analysis as includes the use of the balance and weights, the ordinary operations of filtration, washing, drying, igniting, and weighing of precipitates, the evaporation of solutions, and also the use and calibration of graduated glassware.

A careful study of the first two sections of Fresenius's "System of Quantitative Analysis," the first 40 pages of Treadwell-Hall's "Analytical Chemistry," Vol. 2, and especially Foulk's "Quantitative Analysis," Part 1, is advisable in regard to all these points of manipulation.

In addition to the above a few general precautions and explanations are necessary and should never be overlooked.

In adding reagents to produce any given effect it is important that the right amount be used. To determine what this will be demands a thorough knowledge of what is to take place. In the descriptions of the various processes these amounts are approximately indicated, but it is impossible to provide in this way for all contingencies. Therefore, if the amount of reagent directed fails to do the work it must be increased or diminished as may appear necessary. Thus in every case where a precipitate is formed, it is *essential* that the filtrate be tested by a further addition of the reagent to make sure that the precipitation is complete. This is best done by adding the reagent to a small portion of the liquid in a test-tube, and if a precipitate forms, returning this to the main volume; often a little of the clear liquid over the precipitate can be tested in this way before filtration.

The purity of the reagents, even if marked "c.p.," should always be tested. In many cases it is necessary to run a "blank" determination by going through the process with the reagents alone, leaving out the substance to be tested. The amount of

any impurity which would affect the result can be thus determined and allowed for.

A process should be tested by repeated determinations made on different amounts of the substance. Agreement of the results in this case is a better indication of accuracy than if the same amounts are taken in each determination. Also each process must be tested on material of known composition, such as the Government standards. Every laboratory should have these standards. This cannot be too strongly insisted upon.

The amounts of material prescribed in the descriptions of the processes are those most generally used. They may be changed provided the amounts of the reagents be varied to correspond.

In many of the processes the calculations may be greatly simplified by taking "factor weights" of the material instead of even grams. This consists in weighing out an amount of the substance equal to the fraction that the material to be determined forms of the precipitate weighed. When this is done the weight of the precipitate in grams multiplied by 100 will give directly the percentage sought. If the factor weight is inconveniently large or small some simple multiple of it can be taken and the result estimated accordingly.

For example: one gram of $BaSO_4$ contains 0.137 gram S, and if ten times this factor (1.37 grams) of any substance is taken for the determination of sulfur, each milligram of $BaSO_4$ obtained represents 0.01 per cent. of sulfur. A table of convenient factors of this kind is added at the end of this book and the weights there given may be used, when desirable, in place of those directed in the processes.

A similar method is often used in weighing out material for volumetric determinations when a standard solution is used of which the value of 1 c.c. is determined experimentally and is not an aliquot part of a gram. For illustration see directions for the volumetric determination of lime, page 18.

Every chemist should have a good microscope in his laboratory and use it frequently, especially when unusual or strange material is sent to him for analysis. This will be a great help in showing him the nature of the material and will prevent him from wasting time on useless determinations and from omitting those that ought to be made. The microscope should have the proper

attachment for studying material under polarized light. For metal examination the microscope should have provision for illuminating the object with vertical illumination.

The methods of analysis given in this book are of as universal application as possible. When a large number of determinations of a certain kind are made in a laboratory, the details of manipulation can be arranged so as to save much time and expense. For an exhaustive discussion of this subject see Ridsdale, "Mechanicalizing Analysis as an Aid to Accuracy and Speed for Commercial Purposes," J. Iron and Steel Inst., 1911, No. 1, pp. 332–375, and Proc. Cleveland Inst. of Eng., 1911–1912, No. 4, p. 149.

The acids and ammonium hydroxide solution used in this book are, unless otherwise stated, of the following specific gravities:

Hydrochloric acid,	1.19
Nitric acid,	1.42
Sulfuric acid,	1.84
Ammonium hydroxide,	0.90

METALLURGICAL ANALYSIS

CHAPTER I

THE SELECTION AND PREPARATION OF SAMPLES FOR ANALYSIS

General Principles.—The object sought by the technical analyst is to ascertain the average composition of some particular lot of material—for example, a carload of ore, an ingot of metal or a bin full of coal.

The amount of material treated in the laboratory is of necessity limited to a few grams. The preparation of this small portion so that its analysis shall correctly represent the composition of the mass from which it is taken constitutes the operation of "*sampling.*"

The general mode of procedure is to take from the mass in question several portions selected from different points, and containing coarse and fine material in as nearly as possible the same proportion as they exist in the mass as a whole. This large sample which may weigh from a fraction of a pound to a ton, according to the amount of material the chemist has to examine, as well as to the *extent of variation permissible in the results*, is then crushed to ½ in. or smaller, thoroughly mixed and subdivided by "quartering," until a sample of about 10 lb. is obtained. This is pulverized and all put through a 6-mesh sieve, well mixed and again subdivided, till a sample of 100 to 300 grams is obtained, which is put through an 80- to 100-mesh sieve and bottled for use.

The operation of "quartering" is conducted as follows: The material after being well mixed by shoveling is formed into a pile which is then flattened out by a spiral motion of the shovel. This pile is then divided into four quarters by cutting across at right angles.

Two diagonally opposite quarters are selected and the inter-

mediate ones removed. Care should be taken to brush away carefully all the material of the rejected quarters. The two remaining ones are then mixed together and the operation repeated until a sufficient reduction in bulk is made.

However, if the apparatus is available, it is best to perform the quartering mechanically by a riffle sampler or an apparatus like the Foster-Coolidge automatic sampling machine, especially if many large samples are to be handled. These automatic samplers are more accurate than the hand quartering and much more rapid.

The errors in sampling may be many times larger than those of the chemical analysis, and it is necessary for the chemist to strictly supervise the sampling of the materials which he is to analyze. Otherwise the value of his work may be greatly reduced because of the sample being non-representative of the material it is supposed to represent.

The errors in sampling may be due to faulty methods of taking the sample, as, for instance, taking one or several lumps of ore or coal from a carload when the carload is composed of materials of different composition. Further, it may be very difficult to secure a correct sample because of the heterogeneous composition of the material and the irregular distribution of the different materials of the shipment. Thus, coal is contaminated with slate and pyrite which may be very unevenly distributed. In the sampling of metals the great sources of error are due to segregation of the components of the metal and contamination of the sample with metal and oil from the drill.

In sampling minerals, as coal and iron ore, it is necessary for the sampler to keep in mind the importance of the "size weight" ratio. That is, it is necessary to maintain the sample at all times so large that the loss or gain of a lump as large as the largest lump in the sample and of whatever composition would not affect the accuracy of the sample noticeably. Further, it is necessary that in quartering the sample, the sample be kept crushed so fine that the gain or loss of the largest lump present, of whatever composition, will not noticeably affect the sample. In other words, it is necessary that the sampler be a man of intelligence and that he use his intelligence in sampling.

Many variations from the general procedure will be necessary

with different materials. The following general principles may be stated as a guide:

1. As to the size of the original large sample. This must be greater as the material is less homogeneous and as the importance of the exact determination of any ingredient increases. Thus, a limestone can easily be sampled; but a gold or silver ore consisting of small, detached fragments of a very valuable material in a valueless rock may require the fine crushing of the whole mass of ore and its careful mixing and subdivision, to secure an "average assay."

2. Materials of decidedly different specific gravities require great care to prevent separation into layers during mixing. (Quartering constitutes a fair safeguard against this source of error.)

3. When the ore is sifted, every particle must go through the sieve. The harder parts, which are left unbroken till the last, are often of different composition from the softer and first pulverized portions, and if rejected would cause serious error.

4. Certain ores and slags contain particles of metal which cannot be pulverized. In this case the grains of metal not passing through the sieve must be collected and weighed. The portion passing through the sieve is also weighed. The metal and the siftings are then analyzed separately, and the two analyses combined in the ratio of the relative weights.

Sampling of Metals.—The sampling of metals presents many difficulties. Melted metals can be sampled during pouring by taking a little at the beginning, middle and end of the cast, and averaging the three analyses.

In general it may be stated:

1. Cast ingots are *not* homogeneous. Drillings from different portions will show different analyses. Hence, drillings from a number of points must be well mixed. A single "pig" of cast-iron may vary largely in composition from top to bottom.

2. In tapping a mass of metal from a furnace, different portions of the "run" will show differences in composition. Thus, a "bed" of pig-iron will show wide variations in silicon and sulfur between the top and bottom of the cast.

3. In some metals the operation of drilling will result in a separation; for example, in drilling pig-iron, the fine portion will

be of different composition from the coarse; hence, careful mixing of the drillings is necessary.

Weighing Out from the Laboratory Sample

In this operation the tendency of materials of different specific gravity to separate must never be lost sight of. The substance should be carefully mixed upon a sheet of glazed paper and small portions taken from different parts.

A second source of error is the separation of coarse and fine, as in metal drillings. Great care is necessary to avoid serious difficulty here. The drillings may be moistened with alcohol to make them adherent, and then small portions may be separated, to be subsequently accurately weighed when dry (Shimer).

Dirty pig-iron samples are frequently sent to the chemist, the drillings being contaminated by sand, wood, grease, etc. These may be cleaned from sand with a magnet and from grease by washing with ether, but the analytical results on such samples should never be regarded as entirely satisfactory.

Estimation of Moisture

Many materials (ores, clays, limestones, etc.) as sampled in bulk are often too damp to pulverize. Such samples must be dried on a steam bath or by other means, and the loss of weight determined. The weighing can be done on a portion of the crushed and mixed material which, after drying, is added to the rest of the air-dry sample. It is also always well to determine moisture in the final sample, and allow for it if present. The temperature for drying must not much exceed 100°C., or water of composition may be expelled.

The analysis may be stated on the "dry basis," but should also be calculated on the basis of the wet material.

For example, a cargo of iron ore was sampled in the vessel while unloading, as follows: After the bottom of the boat was reached, portions of the ore were taken every 18 in. from the top to the bottom of the sloping sides of the ore exposed in the hold, including lump and fine in the proportions they formed at each point. This was repeated when the vessel was about half

unloaded. The total amount taken was 200 lb. This was broken up as fine as beans, well mixed by shoveling and divided by quartering until a portion of 10 lb. was obtained, all being done rapidly to avoid loss of moisture.

This portion was weighed.

Weight	9254 grams
After drying in a pan on a steam boiler, weight	8649 grams
Loss	605 grams

This was then pulverized and mixed, and a portion of 100 grams taken for the laboratory. This assayed—

Iron	58.4 per cent.

Then $9254 : 8649 = 58.4 : 54.6 =$ the per cent. of iron in the ore in its original condition.

It may be noted, first, that many ores will absorb water during the pulverization (the amount of water so absorbed will vary with the weather); second, complete drying of a large sample is very difficult; third, ordinary corked bottles are not moisture proof, and samples left in such will change in the course of time, if they are hygroscopic.

In the case of coal, especially the "dry" or non-coking coals and lignites, sampling so as to preserve the moisture in the material unaltered presents many difficulties. Such coals, when pulverized, rapidly lose moisture in dry air at ordinary temperatures, and if then exposed to moist air partially regain it.

The original sample should be rapidly crushed and quartered down, avoiding all unnecessary exposure to air. The final sample can be preserved in rubber-sealed "fruit jars."

In preparing the small fine sample for analysis, speed and covered sieves are necessary. The pulverized material must be kept in bottles with rubber stoppers.

Wet samples, such as coal from a "washer," may be air dried at room temperatures until they can be pulverized, but will not then show, as a rule, the same moisture as the original coal before wetting; hence, if this coal is to be compared with the coal before washing, that should be similarly air dried.

Where much work is done, special ovens for drying samples are of great assistance.

A wooden or cement floor is desirable for quartering large samples, but rubber or oil cloth spread out on the ground can be used.

It should never be forgotten that in grinding hard material with metallic apparatus more or less of the metal will go into the product. Thus, a sample of blast-furnace slag ground in an iron mortar would show more iron than was actually in the slag; therefore for the accurate determination of a small amount of iron in such a material a special sample crushed in agate should be prepared.

Sampling Coal.—In sampling coal as it is unloaded from a car or boat small portions should be taken at regular intervals during unloading. The total amount will vary according to the nature of the coal. Of fine slack about 200 lb. from a car will be sufficient, while if the coal is lump, 500 or 1000 lb. will be necessary. If a number of cars are to be sampled and the analysis of the mixed samples is to be made, a much smaller amount may be taken from each car.

The entire sample should be spread out on a floor and the larger pieces broken with a hammer, unless a power crusher is handy when the entire lot is put through the crusher. The crushed sample is then well mixed and quartered by hand or by a sampling machine and the crushing and dividing repeated until a sample small enough to send to the chemical laboratory is obtained. If the sample has been crushed as small as $\frac{1}{8}$ in. the amount sent to the laboratory need not be larger than 5 lb.

The laboratory sample when received is weighed and thoroughly air dried by exposing in a warm room for about 36 hours or by drying in a drier heated about 10° above the room temperature and with a rapid circulation of air. The sample is then weighed, and the drying continued a half day if mere air drying is done, or two hours if the drier is used. The sample is weighed again and if a loss of not more than 0.2 per cent. is found the drying has been sufficient. The air-drying loss is then calculated in per cent.

The dried sample is then crushed to about 8 mesh and quartered to a pound. It is again crushed to 10 mesh and quartered to $\frac{1}{2}$ lb., and this is then ground on a bucking board or better in a ball mill until it will go through a 60-mesh sieve. A 2-oz. sample

is then put in a rubber-stoppered sample bottle and it is ready for analysis.

The entire sampling, both before and after air drying, must be done as quickly as possible to prevent loss or gain of moisture during the sampling. The sample should not be ground finer than 60 mesh as it then takes up oxygen rapidly. A coarse sample which has been well air dried may lose as much as a per cent. of moisture on being exposed to the air a few minutes after fine grinding. The fine sample must be analyzed promptly even if well stoppered, as it alters rapidly by oxidation and moisture changes.

If the large sample of several hundred pounds first taken is wet or damp it should be weighed and spread out on a floor until dry and weighed again before any quartering is done.

Sampling Iron Ores.—The principles are the same as for coal. It is always best to sample the lot as it is being loaded or unloaded since the material on top may be of different composition from that underneath. At stated intervals of time a shovelful is taken. Or after the ore has been partially removed from the boat or car, leaving cone-shaped depressions, the samples are taken from the faces of these depressions. Thus after a grab has removed as much ore as possible from a hatch, the sampler goes to the face of the cone and, starting from the bottom, he takes trowel samples at stated intervals in a straight line up one side of the cone. This he repeats in four different directions, starting each time from the bottom of the cone. The entire sample from a boat may weigh a thousand pounds.

In sampling cars sometimes a rope net is spread over the car and a sample of several ounces is taken from underneath each knot of the net, of which knots the net will have about 36. The same thing can be done without the net. The ore should not be taken from the surface but far enough underneath to get beyond the reach of surface wetting or evaporation. But it is always best to get the sample from the car while unloading so as to get samples all through the mass of ore.

The sample is weighed if wet, and dried, if not too large, on a steam pan or in a drying oven at 100° and weighed again. This gives the drying loss. It is then crushed to ½-in. size or smaller and divided, crushed smaller and again divided, until the sample

weighs about 5 lb. and is about $\frac{1}{8}$-in. mesh size. This is dried at 100°C. to constant weight, and the loss in weight calculated in per cent. The sample is quartered to about a pound and then ground to 100 mesh in a disc pulverizer having manganese steel discs, or in a ball mill, or on a manganese steel bucking-board. The sample is then mixed well and quartered in a small riffle sampler to about 100 grams and bottled in a rubber-stoppered bottle.

If the original sample is wet and too hard to be dried conveniently, a hundred pounds are accurately weighed and dried at 100°C. for 18 hours and weighed again, and the dry ore added to the rest of the sample which is then treated as above directed. If 100 lb. is too large for the drier, 25 lb. may be taken.

References on Iron Ore Sampling:

Wiley, "Methods used at Illinois Steel Co.," *J. Ind. Eng. Chem.*, III, 103.

Camp, "Methods of U. S. Steel Corporation," *J. Ind. Eng. Chem.*, I, 107.

J. Anal. App. Chem., V, 299.

Glenn, *Trans.* Am. Inst. Mining Eng., XX, 155.

Landis, *Trans.* Am. Inst. Min. Eng., XX, 611.

Kiddie, "Causes of Errors," *Eng. Mining J.*, LXXXVIII, 824.

References on Coal Sampling:

Somermeier, "Coal," pp. 57–79.

Bailey, *J. Ind. Eng. Chem.*, I, 161.

Sampling of Pig-iron.—When the iron is run out of the furnace a spoonful is taken several times during the cast, at least once at the beginning, once at the middle of the cast and once near the end. If the iron is run into ladles it is well to take a spoonful from the middle of each ladleful. The spoonfuls of metal are poured into cast-iron molds about $10\times4\times3$ in. outside dimensions and with inside dimensions of about $6\times1\frac{3}{4}\times1\frac{1}{4}$ in. deep, with a projection in the center so that the ingot will have a notch in order that it may be easily broken to observe the fracture. The ingot should be drilled deeply in at least two places to get drillings for analysis. The drillings from all the ingot samples from a cast are mixed for analysis.

The drill must be worked *dry* (without oil) and care should be taken to reject the outer "skin" of the ingot or bar, which is usually contaminated with matter not properly belonging in the

analysis. Cast-iron is frequently sampled by pouring a little of the molten metal into water. This makes the iron white and very brittle. These so-called "shot samples" and similar brittle material as "spiegel iron" and "wash metal," which are too hard to drill, must be broken into small fragments with a sledge hammer and several pieces pulverized in a steel mortar. A very efficient mortar for this purpose can be made by boring a hole 2 in. deep and 1 in. in diameter into a block of tool steel about 3 in. square and 4 in. high. Fit this with a steel "rammer" cut from a round bar and about 3 in. longer than the hole. It must be only slightly smaller than the hole in the block. Both block and rammer must be well hardened. By dropping a fragment of metal into the hole, inserting the rammer and pounding it vigorously with a heavy hammer the hardest material is soon reduced to a fine sand.

In sampling all metal ingots and billets it must be remembered that the metal will vary in composition from place to place because of segregation, and so must be drilled in several places and if possible clear through.

References on Sampling Metals:

"Methods used by the U. S. Steel Corporation," *J. Ind. Eng. Chem.*, IV, 801.

Shimer, *Trans.* Inst. Mining Eng., XIV, 760.

Keller, "Copper Bar Sampling," *Eng. Mining J.*, XCIII, 703.

Sampling Equipment.—The following or similar equipment is necessary in any laboratory which does a large amount of work:

1. A drill press, preferably a power drill press.

2. A swing hammer pulverizer equipped with a chute for mechanically dividing the samples. The Jeffrey "baby pulverizer," made by the Jeffrey Manufacturing Company of Columbus, Ohio, has a capacity of 1000 lb. of coal per hour reduced to ¼ in. It uses about 7 h.p.

3. A hand or power jaw crusher is especially useful for crushing hard rock, but is also satisfactory for coal crushing to about ¼ in. The "Chipmunk" crusher, made by the Braun Corporation of Los Angeles, will crush 200 lb. per hour to ¼-in. size in the small crusher and 1000 lb. per hour in the large size. About 2 h.p. is required.

4. A pair of 6-in. rolls is needed to crush from ¼-in. size to

10 mesh. The 6-in. rolls made by the American Concentrator Company of Joplin, Mo., can reduce fifty to one hundred 4-lb. samples from ¼ in. to 10 mesh in a day.

5. For reducing the 10-mesh coal samples to 60 mesh or finer a pebble ball mill is very efficient, especially as it prevents moisture changes during the grinding. A four-jar mill such as the one made by The Abbé Engineering Company of New York will grind 40 to 50 samples per day if extra jars are provided.

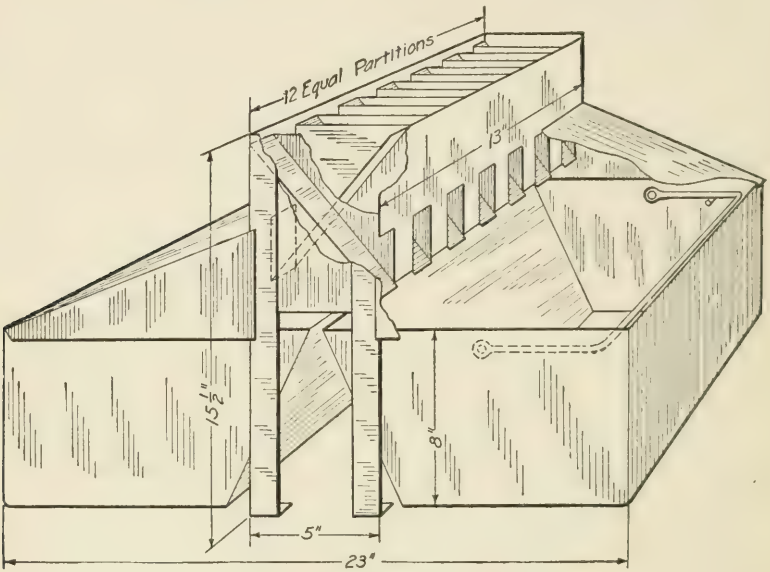

Fig. 1.

6. For occasional sampling a bucking board with heavy muller answers the purpose of fine grinding any mineral sample. It is best made of manganese steel or chrome steel. These steels are so hard that they wear very slowly.

7. A mechanical divider such as the Foster-Coolidge machine is almost a necessity when large numbers of large samples are handled. For samples weighing less than 100 lb. the riffle sampler shown in Fig. 1 answers all purposes unless a large number of samples are handled.

8. Coarse wooden frame sieves from 1 in. to ¼ in. and brass

sieves from 10 mesh to 120 mesh are necessary in the sampling room.

9. For fine grinding of ores an Iler or other disc pulverizer is indispensable if many samples are to be ground.

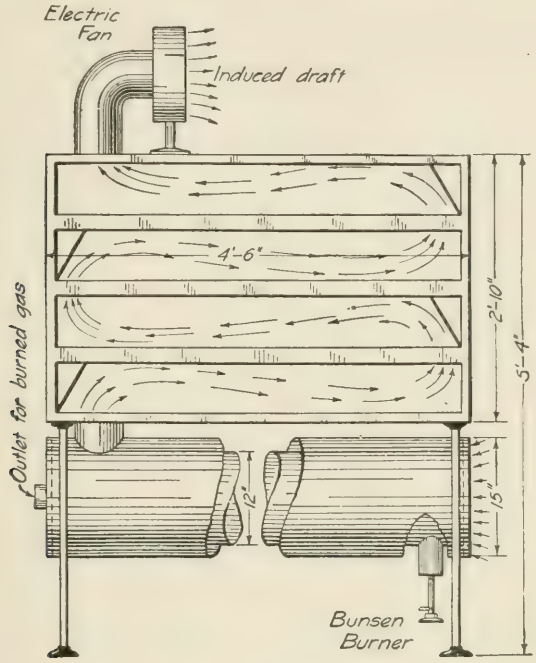

FIG. 2.

10. For drying coarse ores and especially coals the oven shown in Fig. 2 is convenient. A steam-heated pan or table is also useful, especially for wet ores.

11. A large platform scale for weighing up to 1000 lb. and a Troemner solution scale No. 80 for weighing up to 5 lb. are necessary.

CHAPTER II

THE ANALYSIS OF LIMESTONES

The constituents to be determined are silica, oxide of iron, oxide of aluminium, carbonate of calcium, and carbonate of magnesium. The silica is present chiefly as quartz, clay, and other silicates. Beside oxide, iron may be present as ferrous carbonate, or combined with sulfur as pyrite. Small amounts of phosphoric acid and sulfates are also often present, and are determined as in iron ores. Since the water combined in the clay and other constituents such as organic matter are not determined, the results will usually not total up to 100 per cent.

In examining limestone quarries to determine the quality of the stone for furnace flux, lime or cement manufacture, the rock should be sampled layer by layer, as different layers usually vary greatly from each other in composition, while material from the same layer (or "bed") is likely to be of uniform composition. The stone generally ranks in quality according to the carbonate of lime.

Process of Analysis.—Weigh 1 gram of the finely ground sample and transfer it to a platinum crucible. Add 1½ gram of sodium carbonate, and mix well with the sample in the crucible. Then heat cautiously—to prevent spattering due to too rapidly liberated carbon dioxide—and finally heat over a blast or large Meker burner for 10 minutes. Transfer the sintered mass to a casserole, and moisten with water. Clean out the crucible with 30 c.c. of 1:1 HCl, and pour into the casserole. Heat until the cake is dissolved, using a heavy stirring rod to break it up if necessary. It should go completely into solution. Then evaporate to dryness, and heat to 120°C. for one-half hour to render the silica insoluble. Cool the casserole and drench the contents with 20 c.c. of 1:1 HCl, and heat until everything has gone into solution except the silicic acid. Filter on an ashless filter, and wash well (about eight times) with hot dilute HCl, then several times with water. The filtrate will contain perhaps 1 per cent. of the total silica. For exact work, evaporate the filtrate to dryness, dissolve the residue, filter and wash as above. Burn the two

filter papers and their contents together in a platinum crucible, and ignite the silica over a blast for 15 minutes. Weigh the crucible and contents, add a drop of sulfuric acid and 5 c.c. of HF, and evaporate to dryness to expel the SiF_4. Ignite and weigh again. The loss in weight is SiO_2. When great accuracy is not required, and the silica is small in amount, one dehydration may be sufficient and the use of HF may be dispensed with.

After driving off the SiF_4 a small residue of oxides of iron, aluminium, titanium and phosphorus may be left in the crucible. Transfer this residue to the filtrate from the silica by moistening with HCl, and rubbing with a policeman to loosen it, and then washing out of the crucible by means of a jet of water from the wash bottle.

To the filtrate, the volume of which should be about 100 c.c., carefully add NH_4OH until it just smells distinctly of NH_3. Should the precipitate be light colored and large in amount, indicating the probable precipitation of $Mg(OH)_2$, add 5 c.c. HCl and again NH_4OH as before. Now boil the liquid about three minutes or until the odor of NH_3 is nearly gone. Remove from the heat, allow the precipitate to settle, filter on an ashless filter and wash well with a hot 1 per cent. solution of NH_4NO_3. Ignite and weigh the precipitate of Fe_2O_3, Al_2O_3, P_2O_5, TiO_2. If the precipitate of iron and aluminium hydroxides is large, it should be washed from the filter paper back into the beaker, dissolved in HCl, precipitated with ammonia, filtered and washed again. For strictly accurate results, two precipitations should always be made. The iron and titanium may be determined in the ignited precipitate after fusion with $KHSO_4$. For details see the Analysis of Clays, page 298. The P_2O_5 is best determined in another sample, if desired. The sum of the oxides of iron, titanium, silicon and phosphorus when deducted from the total weight of the oxides gives the weight of the alumina.

Dilute the filtrate from the iron, aluminium hydroxide, etc., to about 200 c.c. If it is not distinctly alkaline add 5 to 10 drops of NH_4OH, heat to boiling and slowly add 80 c.c. of a solution of $(NH_4)_2C_2O_4$ also heated to boiling. Use a saturated solution of the salt diluted with an equal volume of water. Stir well during the addition of the reagent and for a minute or two afterward, then set aside until the precipitate of CaC_2O_4 has

settled completely. Decant the liquid through a 9-cm. filter without disturbing the precipitate, wash the precipitate once by decantation, using about 50 c.c. of boiling hot water, then dissolve the precipitate in 5 c.c. HCl, add 100 c.c. water, heat to boiling, add NH_4OH until just alkaline, then 5 c.c. more of $(NH_4)_2C_2O_4$ solution. Let settle, filter, transfer the precipitate to the filter paper and wash six or seven times with hot water. When the filtrate is to be concentrated for the determination of the magnesia, set aside the first filtrate and decanted liquid, and catch the subsequent washings in a separate beaker. Concentrate these by boiling down to a small volume and then add them to the first portion.

Dry the precipitate thoroughly, detach it as far as possible from the filter, put it in a weighed No. 0 porcelain crucible, burn the filter carefully on a platinum wire and add the ash to the contents of the crucible. Now drop concentrated H_2SO_4 on to the precipitate until it is well moistened, but avoid much excess. Heat the crucible (working under a "hood" to carry off the fumes), holding the burner in the hand and applying the flame cautiously until the swelling of the mass subsides, and the excess of H_2SO_4 has been driven off as white fumes. Finally heat to a cherry red for five minutes. Do not use the blast lamp. Cool and weigh the $CaSO_4$. The weight of the $CaSO_4$ multiplied by 0.7350 gives the amount of $CaCO_3$ in the sample, or if multiplied by 0.4119 gives the amount of CaO.

Instead of changing the oxalate to sulfate it is better to place the precipitate and filter paper in a platinum crucible, burn off the paper, cover the crucible with a lid and ignite at the high temperature of the blast lamp or a good Mecker burner for 15 minutes, cool in a desiccator and weigh as CaO. This multiplied by 1.7847 gives the weight of the $CaCO_3$. The CaO should not stay in the desiccator more than an hour before weighing. The blast flame should be inclined, not vertical.

The filtrate from the CaC_2O_4 should be concentrated to 300 c.c. if over that volume; should any MgC_2O_4 separate, dissolve it by adding a little HCl. Add 5 c.c. of NH_4OH, heat to boiling and add 10 c.c. or a sufficient quantity of a saturated solution of Na_2HPO_4. Add a few cubic centimeters more of NH_4OH, then allow to cool with occasional vigorous stirring. The precipitate

of $MgNH_4PO_4$ should be allowed to settle until the liquid is perfectly clear (about two hours). Filter and wash with water containing one-tenth its volume of NH_4OH, sp. gr. 0.90, and a little NH_4NO_3. Ten cubic centimeters of the phosphate solution is sufficient for about 20 per cent. $MgCO_3$; for dolomites more must be added. When there is a large amount of MgO present, the precipitate should be dissolved in a little HCl, made alkaline with NH_4OH and precipitated as before, using only 1 or 2 c.c. of phosphate solution. Dry the precipitate, detach it from the filter paper, and burn the paper on a platinum wire; now ignite the precipitate and filter ash in a porcelain crucible, first heating carefully over a Bunsen burner till all volatile matter is driven off and it has been at a dull red-heat for some minutes, then finishing over the blast lamp for five or ten minutes. The ignited precipitate is $Mg_2P_2O_7$, the weight of which multiplied by 0.7572 gives the $MgCO_3$, or by 0.3621 gives the MgO in the sample.

Notes on the Process.—1. Limestones generally contain silicates. When the sample is heated to a high temperature, silicates of lime and sodium, if sodium carbonate has been used, are formed, which are soluble in HCl with the formation of silicic acid. This is made insoluble by evaporation to dryness, changing the silicic acid into SiO_2 more or less hydrated. The presence of $CaCl_2$ renders the dehydration of the silicic acid easy at the temperature of the water bath. A much higher temperature is to be avoided as silica may recombine with the bases, especially MgO, and so either be redissolved on treatment with acid or render bases insoluble. One evaporation leaves perhaps 1 per cent. of the silica soluble, and even after two evaporations some silica will be found with the iron and alumina precipitate. The silica must be filtered off after each evaporation.

2. The silica retains alkaline salts tenaciously. It must be washed thoroughly, first with hot water acidulated with HCl, then with cold water until the filtrate gives no test for chlorine when tested with $AgNO_3$.

3. The SiO_2 must be ignited to constant weight, as it retains water most tenaciously. A blast lamp is necessary to remove the last traces.

4. $Fe(OH)_3$ and $Al(OH)_3$ are insoluble in solutions of NH_4Cl, but a large excess of NH_4OH holds $Al(OH)_3$ in solution to a slight extent. This is separated by boiling off the excess of NH_4OH or by the presence of a large excess of NH_4Cl. Too much boiling renders the iron and alumina precipitates slimy and difficult to wash and filter. Hence care is necessary in adding the NH_4OH to avoid large excess, so that a few minutes boiling will be sufficient. The precipitate should not be washed

with pure water, as it causes some alumina to go through the paper. The wash solution should be made by adding 20 c.c. of HNO_3, sp. gr. 1.42, to a liter of water and then adding NH_4OH until alkaline.

5. $Mg(OH)_2$ is not completely soluble in NH_4OH unless sufficient NH_4Cl be present to decrease the ionization of the NH_4OH. It separates as a white precipitate easily mistaken for alumina, so if the iron and aluminium hydroxide precipitate is large, it is best to redissolve it in considerable HCl and reprecipitate with NH_4OH. If much iron and alumina are present, the precipitate will certainly contain CaO and MgO which must be removed by re-solution and reprecipitation as above described. Solutions containing NH_4OH and CaO will absorb CO_2 on standing, precipitating $CaCO_3$; hence the iron and alumina hydroxides must be filtered and washed promptly. Distilled water often contains CO_2 which will cause a precipitation in the same way; hence boiling the water before use is best. Cold water in a wash bottle rapidly absorbs CO_2 from the breath; such water should never be used in diluting the alkaline liquid holding the $Fe(OH)_3$ and $Al(OH)_3$ precipitate.

6. Calcium oxalate is very insoluble, but it is a difficult precipitate to filter and wash if not formed exactly right. On gentle ignition below visible redness it is changed to carbonate, and at still higher temperatures to CaO. The complete conversion to oxide requires a rather high temperature for considerable time. However, the change is easily made complete and this method of determining the lime is quite accurate if care is taken to ignite to constant weight. The CaO formed is somewhat hygroscopic and should be weighed as soon as cooled in a desiccator. The action of concentrated H_2SO_4 on calcium oxalate converts it to $CaSO_4$. The action is not violent and the excess of H_2SO_4, provided it is moderate, can be driven off without danger of loss by spurting. Lumps in the crucible should be broken up before H_2SO_4 is added and care should be taken that the entire mass is moistened by the H_2SO_4. $CaSO_4$ will stand the cherry red heat of a Bunsen burner without alteration, but the higher heat of a blast lamp will cause it to lose SO_3.

It must not be forgotten that any strontium in the sample will precipitate with the calcium as strontium oxalate.

7. Calcium oxalate is somewhat soluble in hot water, hence care should be taken not to use unnecessarily large amounts of hot water in washing it.

8. Magnesium will precipitate as oxalate in concentrated solutions, hence when much is present the calcium oxalate should be dissolved and reprecipitated as described above. In the case of ordinary limestone, this is not necessary if the calcium is precipitated in properly diluted solutions, unless very accurate results are desired.

9. On concentrating the filtrate from the calcium oxalate, a crystalline precipitate of magnesium oxalate will sometimes separate. This can be redissolved in HCl and added to the solution. If it contains any calcium oxalate it will leave a milky solution clearing slowly.

10. As the liquid in which the magnesium is precipitated contains all the material added in the analysis, careless addition of reagents may give so strong a solution of ammonium and sodium salts that the precipitation of the magnesium phosphate will not take place promptly. However, the precipitation will be complete in time. To get rid of the ammonium salts, the filtrate should be evaporated to dryness with 3 c.c. of HNO_3, sp. gr. 1.42, for each gram of NH_4Cl, which will decompose and remove ammonium salts. Then any remaining magnesium may be precipitated.

11. There must be enough $(NH_4)_2C_2O_4$ solution added to convert all the magnesium as well as the calcium to oxalate or calcium oxalate will not completely precipitate.

12. Sodium oxalate being very sparingly soluble will sometimes separate with the magnesium precipitate, especially when the solution is concentrated and much Na_2HPO_4 has been added; in this case, after partial washing, the precipitate must be dissolved in HCl and reprecipitated by NH_4OH.

13. Any manganese which was in the sample will precipitate chiefly with the magnesium. It can be determined very accurately in the ignited precipitate colorimetrically and the magnesium results corrected. Any barium in the sample will be found chiefly in the filtrate from the magnesium, but some will be with the calcium and some perhaps with the magnesium.

References:

"Silica Separation," *J. Anal. and App. Chem.*, Vol. IV, p. 159.

"Magnesium Calcium Separation, Fresenius, Quantitative Analysis," Pars. 73, 74, 101, 104, 154.

For refined methods of limestone analysis see United States Geological Survey *Bulletin* 422, "The Analysis of Silicate and Carbonate Rocks," by W. F. Hillebrand.

Instead of determining the total silica as is given in the above process, it is the custom in many places to determine what is called the "insoluble silicious matter." This is done by dissolving the sample in strong HCl, evaporating to dryness to dehydrate any soluble silica, and then filtering off, washing and weighing the residue. Iron and alumina, lime and magnesia are then determined in the filtrate as in the filtrate from the silica. The insoluble silicious matter, however, generally is not all silica. Since it is just about as quick to ignite and determine

silica accurately, the determination of "insoluble silicious matter" seems hardly worth while.

The determination of CO_2 is generally not necessary for technical purposes, but it may very easily be done by use of the apparatus shown on page 104. A 1-gram sample is placed in the flask, covered with water, and HCl added slowly so that not more than three or four bubbles per second pass through the KOH bulb. When effervescence ceases, the acid in the flask is heated to boiling, and then a liter of air is drawn through the apparatus. The increase in weight in the KOH bulb gives the amount of CO_2. The KOH bulbs must of course show no increase or decrease in weight when a liter of air is aspirated through as a blank before the regular determination.

The Volumetric Determination of Lime

Instead of weighing the calcium as $CaSO_4$ or CaO, it may be determined by measuring the volume of a standard solution of $KMnO_4$ required to oxidize the oxalic acid which it contains. The precipitate is first dissolved in dilute sulfuric acid, the liberated oxalic acid is then titrated by $KMnO_4$. The reactions may be summed up as follows:

$$5CaC_2O_4 + 8H_2SO_4 + 2KMnO_4 = 5CaSO_4 + K_2SO_4 + 2MnSO_4 - + 10CO_2 + 8H_2O.$$

This reaction takes place rapidly at 70°C. The first few drops of permanganate color the liquid and a few seconds will elapse before color disappears, then the reagent may be added rapidly. This delay in starting is entirely removed if a few drops of a strong solution of $MnSO_4$ are added to the liquid before titration. As the titration proceeds, rapid effervescence of CO_2 takes place, resulting in a spraying out of some of the liquid unless the titration is done in a flask.

Solution Required.—The solution required is a standard solution of potassium permanganate. The same solution can be used as for the determination of iron in ores. The iron value multiplied by 0.8960 gives the $CaCO_3$ equal to 1 c.c. of permanganate in the above reaction; however, it is best to standardize the permanganate against pure Iceland spar or pure lime, which is dissolved in HCl, and the calcium precipitated as oxalate as in the above process.

Process.—A. For limestone low in magnesia.

Weigh out 89.6 times the iron value of the permanganate, if it is desired to report as carbonate, or 50.2 if it is desired to report as CaO. The sample should be finely ground. Transfer to a

small platinum crucible, and ignite cautiously to destroy organic matter. Transfer the ignited powder to a 400 c.c. beaker, add 20 c.c. of water, cover and then add 15 c.c. HCl, sp. gr. 1.19, and 3 or 4 drops of HNO_3. Boil until all the soluble matter is dissolved and all the CO_2 expelled. Wash off and remove the cover and dilute the liquid to about 150 c.c. with water free from CO_2. Add NH_4OH in slight excess, and heat to boiling. Then without filtering off the precipitated iron and aluminium hydroxides, precipitate the CaC_2O_4 exactly as in the gravimetric analysis. Continue the stirring two or three minutes after the addition of the hot ammonium oxalate solution and then let settle until nearly clear, which should require not over five minutes if the work is correctly done.

Decant through a 9 cm. filter, pouring off very closely. The precipitate should be so dense as to render this easy. Add 30 c.c. of hot water to the precipitate, stir well, let stand three or four minutes, and again decant. Repeat the decantation a third time and then transfer the precipitate to the filter and wash about eight times with hot water.

Reserve the filtrate and washings for the determination of magnesia.

Now run 10 c.c. of water through the filter and catch it in a small beaker, add ½ c.c. sulfuric acid, heat to 70° and add a drop of standard permanganate solution. If the color is not discharged in two or three minutes, the precipitate is sufficiently washed; otherwise continue the washing and test again. Then wash the CaC_2O_4 back into the beaker in which it was precipitated, add water if necessary to make a volume of at least 150 c.c., place the beaker under the funnel and run through the filter into the beaker 30 c.c. of 1:3 H_2SO_4. Stir the contents of the beaker thoroughly while the acid runs in to avoid the separation of $CaSO_4$. Now wash the funnel and filter thoroughly with hot water. Dilute the liquid in the beaker to 350 c.c., heat to 70°C. and titrate with permanganate to a faint pink color not disappearing in two or three minutes.

To test the filter paper for undissolved CaC_2O_4, it may be added to the contents of the beaker and stirred up in it; if the washing has been careful, it will not cause the discharge of the color.

If the factor weight was used, the number of cubic centimeters of the permanganate required for the titration will equal the percentage of $CaCO_3$ or CaO in the sample, for if 1 c.c. equals 0.01 gram Fe, it will equal 0.00896 gram $CaCO_3$ or 0.00502 gram CaO, and if 100 c.c. were used it would be equal to 0.896 gram $CaCO_3$ or 0.502 gram CaO, which were the samples to be taken.

The CaC_2O_4 obtained in the first method given, instead of being weighed as $CaSO_4$ or CaO, may be dissolved and titrated by permanganate as in the volumetric process.

When magnesium is present in considerable amount two precipitations of the CaC_2O_4 must be made, for the same reason that two precipitations are required in the gravimetric process when magnesia is high, *i.e.*, because the CaC_2O_4 will carry down with it some MgC_2O_4. If two precipitations are to be made it is necessary to filter off the $Fe(OH)_3$ separately, as it will be reduced by the oxalic acid when the CaC_2O_4 is dissolved in HCl and interfere with the magnesia determination.

Notes on the Process.—Ignition of the sample is necessary to destroy any organic matter present, which if not destroyed will reduce $KMnO_4$ and cause the calcium results to run high.

Unless the precipitate of CaC_2O_4 is stirred up in a considerable volume of water, when the first few cubic centimeters of sulfuric acid are added to dissolve it, a dense flaky precipitate of $CaSO_4$ may separate which is likely to occlude solution and obscure the end point.

If the $KMnO_4$ is added too rapidly during the titration or the solution is not well stirred, brown MnO_2 may separate out; if this is not redissolved the results will be inaccurate.

All water used in diluting the solutions in this process for lime must be free from CO_2, or $CaCO_3$ will come down with the CaC_2O_4, and as this does not react with the permanganate, the lime will run low. For the same reason it is important that all CO_2 be expelled from the solution of the sample in HCl by boiling it thoroughly.

References on Volumetric Determination of Lime and Magnesia:
Fresenius, "Quantitative Analysis."
Sutton, "Volumetric Analysis."
Handy, *J. Am. Chem. Soc.*, 1900, p. 31.
Meade, *J. Am. Chem. Soc.*, 1899, p. 746.
Ulke, *Eng. Mining J.*, 1900, LXIX, p. 164.
Konnick, *J. Soc. Chem. Ind.*, 1900, p. 564.
For the conditions for the titration of oxalate by permanganate see McBride, *J. Am. Chem. Soc.*, 1912, p. 393.

The Determination of Free Lime

This is based on the fact that uncombined CaO forms soluble compounds with sugar in solution in water and that calcium carbonate, alumina, ferric oxide, magnesium carbonate and free magnesia do not dissolve. The writer has carefully tested the effect of the presence of free magnesia upon this determination of free lime and finds that it is without influence.

The method is very convenient for the determination of free lime in burnt and hydrated limes.

Process of Analysis.—Place 1 gram of the finely ground sample in a 200 c.c. flask, add 15 grams of cane sugar and 50 c.c. of water and shake the flask vigorously for several minutes. Dilute to the mark, mix the solution thoroughly and let the residue settle until the solution is clear, pipette off 100 c.c. and titrate the lime with standard HCl, using phenolphthalein as indicator. If the HCl is N/5, each cubic centimeter is equal to 0.005607 gram of CaO. Phenolphthalein is prepared as directed on page 57.

To prepare the N/5 hydrochloric acid proceed as follows: Dilute 17.0 c.c. of HCl, sp. gr. 1.19, to 1 liter and standardize exactly as directed on page 57 for the standardization of HNO_3, except that 0.53 gram Na_2CO_3 should be weighed; or ignite 2.002 grams of pure, dry, powdered Iceland spar ($CaCO_3$) in a platinum crucible over a Meker burner until constant weight is attained, dissolve completely in sugar solution as directed above, dilute to 200 c.c., pipette off 50 c.c. and titrate with the acid to be standardized. If the acid is exactly N/5, 50 c.c. will be required. If the acid is too strong, as it will likely be, dilute the calculated amount and titrate again.

Note.—Hydrochloric acid makes the best standard acid for general use because it forms readily soluble salts with all the radicals commonly titrated with acids, is easily obtained pure, the strength of the acid is easily verified by means of silver nitrate, the dilute solutions used suffer no appreciable loss when boiled, and the strength of the acid does not change on keeping.

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- Stone and Schenk, *J. Am. Chem. Soc.*, 16, 721.
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Mellor, "Quantitative Analysis," 527.

CHAPTER III

THE DETERMINATION OF IRON IN ORES

Many iron ores give up practically all of their iron to hydrochloric acid, provided that the acid be strong and the ore be very finely pulverized. On the other hand, many ores contain a small amount of iron in such a state of combination that it will not dissolve in hydrochloric acid. In such cases the residue after treatment with acid must be fused and the iron determined in the fusion.

If the residue after treatment with HCl is pure white with no dark specks, the iron is probably all dissolved unless the ore contains TiO_2, in which case an insoluble compound of iron, titanium and phosphorus may remain which will not color the residue.

Sometimes previous ignition of the ore will cause the ore to dissolve more completely in acid.

All methods for the determination of iron in ores depend upon reducing the iron in acid solution to the divalent form, then measuring the amount of a standard oxidizing agent required to oxidize the iron back to the trivalent condition. The reducing agents are metallic zinc, metallic aluminium, $SnCl_2$, H_2S, SO_2. The oxidizing agents are $K_2Cr_2O_7$ and $KMnO_4$.

The Determination of Iron by Potassium Dichromate after Reduction of the Ferric Chloride by Stannous Chloride

The process depends upon the following reactions:

1. A strongly acid solution of $FeCl_3$, if boiling hot, is almost instantly reduced to $FeCl_2$ by a solution of $SnCl_2$, the end of the reaction being shown by the disappearance of the yellow color of the ferric ion.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

2. Any slight excess of stannous chloride can be removed by adding $HgCl_2$, forming a white precipitate of HgCl which is without action on iron salts or dichromate, the stannous chloride being oxidized to stannic chloride by the $HgCl_2$.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$

The reaction is not instantaneous, and after the addition of the $HgCl_2$ at least two or three minutes should elapse before titration. The reaction is satisfactory, provided not too much $SnCl_2$ is present and the $HgCl_2$ is in large excess and added all at once. Otherwise metallic mercury may be formed as a gray precipitate which will act on the dichromate and cause false results. Thus, $SnCl_2+HgCl_2=SnCl_4+Hg$. This reaction is at once detected by the gray color of the precipitate and entirely vitiates the results. If the solution is very hot the difficulty of avoiding reduction to mercury is increased.

3. When a solution of potassium dichromate is added to a solution of $FeCl_2$ containing a considerable excess of HCl, the $FeCl_2$ is immediately oxidized to $FeCl_3$ with a corresponding reduction of dichromate to $CrCl_3$ giving a green color to the solution. The reaction is,

$$K_2Cr_2O_7+14HCl+6FeCl_2=2KCl+2CrCl_3+6FeCl_3+7H_2O.$$

In the absence of an excess of HCl the solution becomes yellowish instead of green, and more HCl must be added, otherwise error will be made.

4. The end point, that is, the completion of the oxidation, is determined by the use of potassium ferricyanide. When a drop of the solution containing a ferrous salt is added to a drop of a dilute solution of ferricyanide an intense blue color is produced, while solutions containing only ferric salts give a yellow-brown color with ferricyanide. The ferricyanide solution must be fresh, as it is reduced on exposure to light or on standing, with a formation of ferrocyanide, and of course the salt must be pure; some ferricyanide is contaminated with ferrocyanide, which gives a blue color with both ferric and ferrous iron and consequently cannot be used.

Preparation of the Solutions. 1. Potassium Dichromate Solution.—Place a platinum crucible containing a sufficient quantity of dichromate in a sand-bath with the sand as high on the outside as the dichromate on the inside of the crucible. Heat until fusion of the dichromate just commences around the sides of the crucible. Then remove the crucible.

Weigh out exactly 8.779 grams of the cold powdered dichromate; dissolve in 300 c.c. of cold water, transfer to a liter flask, dilute to 1 liter, and shake well to insure thorough mixing. One cubic centimeter of this solution should oxidize exactly 0.01 gram of iron from ferrous to ferric condition.

Now to test the solution dissolve 2.81 grams of pure ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_26H_2O$, in 75 c.c. of water containing 7 c.c. of HCl. The salt contains 14.24 per cent. Fe and

should require just 40 c.c. of the dichromate solution to titrate it. Run in from a burette 39 c.c. of the dichromate solution, stir well and add a drop of the solution to a drop of the ferricyanide solution placed on a white porcelain plate. A blue color forms if ferrous iron is present. Now add the dichromate solution drop by drop, testing the liquid after each addition until on testing with ferricyanide a yellow color is produced instead of a blue after one-half minute. If the burette is properly calibrated and the dichromate properly made the liquid in the burette should now read 40 c.c. If it does not, repeat the test and make a factor of correction. For example: If instead of 40 c.c. of dichromate 40.2 were required, the strength of the dichromate in terms of iron would be $\frac{40}{40.2} \times 0.01 = 0.0099502$ gram per cubic centimeter. For volume corrections see table 8, page 325.

The object of the heating of the dichromate is to expel water and destroy any trace of organic matter present.

If the salt is strictly pure and the fusion has been carefully conducted it will dissolve to a perfectly clear liquid which will check exactly with the iron salt if this is also pure. This makes a double check on the solution and the results obtained by the two methods should closely agree. Of course the burette used must be carefully calibrated.

Some of the dichromate on the market contains excess of chromic acid, and gives too strong a solution. When this is true the salt should be purified by recrystallization. If the salt is heated too hot, especially if it is not pure, the solution will be turbid. If more than a trace of this turbidity shows, a new solution should be prepared.

2. **Stannous Chloride Solution.**—Dissolve stannous chloride in four times its weight of a mixture of three parts of water and one of HCl, sp. gr. 1.2. Add scraps of metallic tin and boil until the solution is clear. Keep this solution in a closed dropping bottle containing metallic tin.

3. **Saturated Solution of Mercuric Chloride.**—Keep an excess of salt in a bottle and fill it up with water from time to time.

4. **A Very Dilute Solution of Potassium Ferricyanide.**—Dissolve a piece half as big as a small pea in 50 c.c. of water. This solution must be made fresh when wanted as it does not keep.

The other solutions keep indefinitely. The $SnCl_2$ solution, however, absorbs oxygen from the air and hence must be kept closed. Should it grow turbid or deposit a white precipitate, add more HCl and metallic tin and heat until clear.

Process for the Analysis.—Pulverize the ore in an agate mortar until it is so fine that no grit can be felt between the teeth. It is best to grind a small amount at a time.

Weigh out 1 gram; put it into a small dry beaker, brushing off the watch-glass carefully. Add 25 c.c. HCl, sp. gr. 1.2, cover the beaker with a watch-glass and set it on a hot plate. Digest at a temperature just short of boiling until all iron is dissolved and on shaking the beaker the residue appears light and flotant, and free from dark heavy particles. This may take from 15 minutes to an hour or more according to the nature of the ore. Dilute the solution to two or three times its original volume, filter through a small filter into a 250 c.c. beaker, and wash the residue on the filter until it is free from acid. Heat the solution to boiling, drop in the tin solution slowly until the last drop makes the solution colorless, indicating complete reduction. If too much stannous chloride is dropped in by mistake, add permanganate to the solution until a yellow color appears, then again add stannous chloride drop by drop until the yellow just disappears. Dilute with cold water to 200 c.c., then add all at once, with vigorous stirring, 15 c.c. of the mercuric chloride solution. Let stand three or four minutes. A slight white precipitate should form. If none, or a heavy grayish precipitate forms, the result is rendered doubtful and the determination should be repeated.

Divide the solution into halves approximately. Into one-half run in the standard dichromate solution until the end point is roughly obtained, then add the other half, washing the solution out of the beaker thoroughly and complete the titration accurately. The final end point is known approximately from the end point obtained on the first half of the solution. In this way it is not necessary to consume much time approaching the end point. The number of cubic centimeters used multiplied by the iron factor of the dichromate and then by 100 gives the percentage of iron in the sample.

If by any accident too much of the dichromate solution is run

in, add 1 c.c. of a dilute solution of ferrous sulfate, finish the titration and read the burette. Then add 1 c.c. more of the same solution, again finish the titration and read the burette. Deduct the difference between the first and second readings from the first reading to find the true end point.

Notes on the Process.—When an ore is with difficulty decomposed by HCl, the addition of 2 or 3 c.c. of $SnCl_2$ solution to the ore and acid in the beaker will greatly accelerate the solution of the ore. In this case, after the color and nature of the residue shows complete extraction, carefully add a solution of $KMnO_4$ to the contents of the beaker until the yellow color of ferric chloride again appears, then dilute and proceed as usual. The object of the permanganate is to oxidize the excess of stannous chloride.

In the case of unknown ores, or of an ore in which not all of the iron can be completely dissolved by HCl, the residue after solution in HCl must be fused to render soluble the rest of the iron. Place the filter in a platinum crucible, burn off the paper, add 2 or 3 grams of $KHSO_4$ and fuse over a Bunsen burner until all iron is extracted. Dissolve the fusion in 50 c.c. of water and 5 c.c. of HCl, heat to boiling, add a drop of stannous chloride solution and then place a drop of the solution on a white plate and test for ferric iron with KCNS. If a red color is produced more stannous chloride is needed, but the chances are that not more than one drop of stannous chloride will be required. The reason for using KCNS is that after fusion in platinum some platinum always goes into solution, and stannous chloride produces with this a yellow color, so that the end of the reduction cannot be told by the disappearance of the yellow color of ferric chloride.

Now add $HgCl_2$ and titrate as in the case of the main solution.

There is danger of loss of iron if a concentrated solution of $FeCl_3$ in HCl is boiled; hence too great concentration of the solution and too hard boiling must be avoided.

In testing the solution to see if the end point is near, care should be used that only very small drops of the solution which is being titrated are removed, otherwise an appreciable amount of untitrated iron may be taken out, causing low results. As the end point is approached the blue color obtained when the test is made with ferricyanide grows less intense until the addition of one more drop of dichromate to the iron solution gives a test with no trace of green color.

In the case of mill cinder and other decomposable slags, add 20 c.c. of water to the finely powdered material, and stir up well to prevent the cinder caking on the bottom of the beaker; then add 25 c.c. HCl and proceed as before.

Titanium will not affect this process, provided care be taken to fuse the residue and add the solution of the fusion to the main solution. When zinc is used to reduce the iron, titanium is also partly reduced.

The presence of vanadium will vitiate the results as it is reduced by $SnCl_2$ and oxidized by dichromate.

The porcelain plate upon which the tests for the end point are made should be prepared by warming a plate on a steam-bath, then rubbing with a piece of paraffin so as to cover the whole plate with a thin skin of paraffin. The test drops will not then spread over the plate.

The Determination of Iron by Titration by Potassium Permanganate after Reduction by Metallic Zinc

This is a widely used process. The time of the actual titration is shorter than with the dichromate, as an outside indicator is unnecessary because the permanganate acts as its own indicator. The least bit of permanganate added to the solution in excess of that required to titrate it gives to the solution a permanent pink color.

On the other hand, the permanganate is much more liable to change than the dichromate and is also much more subject to reduction by other materials, as for example, organic matter in the ore or solution.

Titration by permanganate in HCl solution is only permissible under certain closely regulated conditions. The amount of HCl must be small and a certain amount of manganese salt must be present, otherwise the HCl will cause some reduction of the permanganate, giving a brown color to the solution and making the results run too high. The presence of phosphoric acid is desirable as it changes the yellow ferric chloride to colorless ferric phosphate, thus making the end point plainer. The phosphoric acid is also said to prevent the reduction of permanganate by the HCl.

Reduction of the iron by zinc is accomplished either by adding granulated zinc to the solution in an Erlenmeyer flask and boiling a few minutes or by using the "reductor" introduced by Mr. Clemens Jones, in which the iron solution is filtered through a column of amalgamated granulated zinc.

Zinc is such a powerful reducing agent that many substances are reduced by it to oxidizable forms which vitiate the result. Thus the iron solution must not contain arsenic, titanium, vanadium, or nitrates, since lower oxides are formed which are oxidized by permanganate. Nitrates are reduced ultimately to ammonia which does no harm, but frequently the reduction is only partial resulting in the formation of hydroxylamine (NH_2OH) which is oxidized by permanganate. The

writer has known of results for iron running as high as 125 per cent. because the H_2SO_4 used had in it HNO_3 which was reduced to NH_2OH.

As the zinc is never pure, a blank must be run on it and the amount obtained subtracted from the permanganate used in the regular titration. If pure zinc is used without being amalgamated with mercury the zinc used must be completely dissolved each time as it reduces some iron on it as metallic iron, making the result run low. When the zinc is amalgamated the reduction is much less powerful, in fact if the mercury coating is too heavy the reduction of the iron is apt to be too slow. There should be not more than 5 per cent. free acid present.

The reactions involved are: $Zn + Fe_2(SO_4)_3 = ZnSO_4 + 2FeSO_4$. $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$.

Solution Required. Permanganate Solution.—A convenient solution is one in which 1 c.c. equals 0.01 gram of iron, *i.e.*, one which has in 1 c.c. sufficient permanganate to oxidize 0.010 gram of iron from divalent to trivalent condition. This will contain 5.659 gram of $KMnO_4$ to the liter.

To prepare the solution, dissolve 5.7 grams of pure permanganate of potassium in water, and when dissolved dilute to 1 liter. The solution should stand a day or so before being standardized. It is likely to alter rapidly at first, but in time reaches a comparatively stable condition if protected from light and dust. Where large quantities are used it is a good plan to make up a carboy ahead and let it be "ageing." The container should be painted black to keep out light.

Standardization of the Permanganate.—The reducing reagents used as standards are: Pure iron wire, ferrous ammonium sulfate, sodium oxalate and oxide of iron or iron ore in which the iron content is known. It is best to standardize against several of these reagents and the results should agree closely. If they do not, purer materials should be obtained.

To standardize against iron wire proceed as follows: Clean the wire by rubbing it with emery cloth and then with filter paper. Form it into a spiral by wrapping it around a clean glass rod and cut the spiral into lengths weighing about 0.4 gram. Throw away the part of the wire which was held by the fingers. Accurately weigh the pieces and put them into small Erlenmeyer flasks of about 75 c.c. capacity. Close each flask by a small glass bulb with the stem reaching down into each neck. The glass bulb

prevents air entering the flask and oxidizing the iron. Add 30 c.c. of H_2SO_4 (1:4) and set the flask on a hot plate until the iron dissolves, avoiding violent boiling. When the iron is completely dissolved, pour cold water over the bulb into the flask, thus washing both the bulb and the neck of the flask. Transfer the solution to a beaker, dilute to 200 c.c. and titrate without delay. The weight of the wire taken multiplied by the iron factor of the wire and divided by the number of cubic centimeters of the permanganate used will be the amount of iron equivalent to 1 c.c. of the permanganate. The result may be checked by running the titrated solution through the reductor and again titrating. With the "blank" deducted, the results ought to check. The wire is usually about 99.8 per cent. iron.

Now, knowing the strength of the solution it may be diluted so that 1 c.c. will just equal 0.0100 gram of iron. The water used for diluting should have been boiled and, while boiling, treated with permanganate until it retains a very faint pink color.

In all work involving the use of permanganate, glass stop-cocked burettes should be used, as it is reduced by rubber.

To standardize with ferrous ammonium sulfate or sodium oxalate, weigh 2.81 grams of the sulfate or 0.4799 gram of the oxalate, transfer to a 300 c.c. flask, add 250 c.c. of hot water containing 8 c.c. of strong H_2SO_4 and titrate not too rapidly, approaching the end point slowly. In the case of the oxalate the titration should be carried on at 70°C.

The amounts of sulfate and oxalate given above are each equal to 0.400 gram of iron. The reason this amount is chosen is that it is about the amount of iron that will ordinarily be titrated in a sample of ore and consequently no end-point correction will have to be made. The end color obtained in standardization should be of the same depth as when a sample of ore is titrated.

2. **Titrating Solution.**—This is made by dissolving 160 grams of manganous sulfate in water, diluting to 1750 c.c., adding 330 c.c. of phosphoric acid and 320 c.c. of sulfuric acid. Use the concentrated "syrupy phosphoric acid" of 1.725 sp. gr.

Preparation of the Reductor.—A simple form of the reductor is shown in Fig. 3. The large tube is about $\frac{5}{8}$ in. inside diameter and is contracted at the bottom and expanded into a funnel at the top. The stem enters the rubber stopper of the flask, which

is connected to a suction pump. The tube is filled as follows: A plug of glass wool is placed in the bottom. Above this is ¾ in. of clean white sand B, which has been boiled with HCl and then washed to remove the iron. Above the sand is a disc of perforated platinum C. Above this the tube is filled for 10 in. with granulated zinc of such size that it will pass through a 20-mesh sieve but not through a 30-mesh. It should be amalgamated as follows: Moisten a quantity of it with very dilute H_2SO_4 (about 3 c.c. to 100 c.c. of water), add a small drop of mercury and stir it in until the zinc shows uniformly the white mercury color. Wash the zinc free from acid and put it in the tube. Avoid more than just enough mercury. One-half gram is sufficient for 150 grams of zinc.

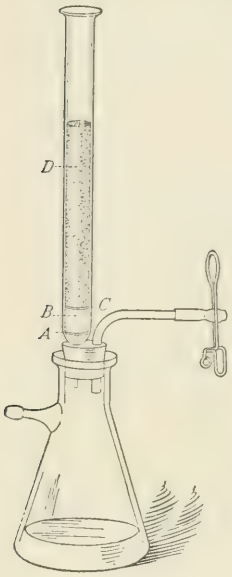

FIG. 3.

The solution to be reduced is poured into the funnel-shaped top of the reductor. The rate at which it is drawn through must not be too rapid. Test this point by drawing an iron solution through and then adding some ammonium sulfocyanate to the reduced solution. If this gives a pink color the speed was too great and must be reduced by diminishing the suction. If the rate is too fast it can be reduced by opening the pinch-cock. If air is drawn through the zinc in the reductor and immediately followed by dilute acid, the liquid running through is sometimes found to be oxidizing, possibly from the formation of H_2O_2; hence while running through the solution and wash water, the surface of the zinc must be kept continually covered with liquid.

If the reductor has stood unused for some time it should be washed out with dilute sulfuric acid and water before putting the solution through it.

Process of Analysis.—Weigh out 1 gram of the finely ground sample and ignite it in a porcelain crucible to destroy organic matter. Transfer it to a small beaker, add 10 c.c. of concentrated HCl, cover and digest till all the iron is in solution. Add 20 c.c.

of dilute H_2SO_4 (1 : 1) and boil gently to expel some of the excess of HCl, then dilute to about 100 c.c. and filter, washing the residue thoroughly. Dilute the filtrate to 250 c.c., using cold water, as the solution should be cool.

Now pour the solution into the zinc reductor and apply such suction that the liquid will flow through in a moderate stream. Follow the solution with 100 c.c. of 5 per cent. H_2SO_4, then with 150 c.c. of water, keeping the zinc covered with liquid during the entire process so that air will not be drawn through the zinc. As soon as the last wash water has passed through, disconnect the suction tube, pour the solution into a large beaker and rinse the flask out with a little water. Add 10 c.c. of the titrating solution and titrate with $KMnO_4$. The number of cubic centimeters of the $KMnO_4$ times the iron factor, times 100 equals the percentage of iron.

Notes on the Process.—Ignition of the sample is necessary unless organic matter is known to be absent.

The gentle boiling, after adding the dilute H_2SO_4 gets rid of most of the HCl. It is not necessary to expel all of it.

Determine the correction of the impurity in the zinc by running a blank with the same amount of water and acids used in the analysis, and deduct the volume of permanganate required in this from that used in the analysis.

The process should be checked on ores of known composition.

The Permanganate Method with Reduction by Stannous Chloride

This method is reliable provided the conditions of titration are strictly controlled. A very slight excess of $SnCl_2$ must be used, the amount of HCl present must not be more than is directed, the solution to be titrated must be cold and dilute. In strongly acid solutions HgCl and HCl are acted upon by permanganate. The permanganate should not be added too rapidly, especially toward the end. Organic matter and sulfides must be destroyed by ignition of the ore.

Process of Analysis.—Weigh 1 gram of the finely ground ore, transfer it to a crucible and ignite to redness. Transfer to a beaker, add 20 c.c. of HCl (1 : 1). Heat until the iron is all dissolved. To hasten the solution, $SnCl_2$ may be added at this point until the solution becomes colorless. Now if an excess of

$SnCl_2$ has been added, add permanganate until the yellow color of ferric iron appears, then to the hot solution very carefully add $SnCl_2$ solution until the yellow just disappears. Cool thoroughly, add 10 c.c. of saturated $HgCl_2$ solution, stir well and allow to stand for several minutes. Dilute to 250 c.c. with water free from reducing matter, add 10 c.c. of the "titrating solution," and titrate not too rapidly with permanganate. Approach the end point rather slowly. The last drop should give a persistent pink color.

Note.—Instead of using $SnCl_2$, zinc, aluminum, or SO_2 can be used to reduce the iron, and then according to Hough, the only reagent necessary to add to make the titration accurate is phosphoric acid.

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Camp, "Methods of Sampling and Analysis of Iron Ores," *J. Ind. and Eng. Chem.*, Vol. I, No. 2, p. 107.

Determination of Ferrous Oxide in Iron Ore

This determination is not frequently called for, but in the case of carbonate ore, $FeCO_3$—or magnetite ore, Fe_3O_4—it is sometimes necessary in order to calculate the heat balance of a blast furnace. The ferrous oxide is also determined to test the completeness of calcination of carbonate ore.

When ores of iron are dissolved in HCl, ferric oxide goes in solution as $FeCl_3$ while ferrous oxide or ferrous carbonate go in solution as ferrous chloride. Thus:

$$FeCO_3 + 2HCl = FeCl_2 + H_2O + CO_2.$$

The $FeCl_2$ can then be titrated by any of the ordinary methods.

An accurate determination of ferrous oxide can be made only when certain possible constituents of ores are absent. Some organic material, and all decomposable sulfides, will reduce ferric to ferrous iron and cause the results to run high. On the other hand any MnO_2, such as pyrolusite, will liberate chlorine when the ore is dissolved in HCl and this will oxidize the ferrous iron to ferric, making the results for FeO low.

Process of Analysis.—Fit a 150 c.c. flask with a clean rubber stopper perforated with one hole, in which is inserted a piece of glass tubing 2 in. long. Upon this slip a piece of pure gum tubing 3 in. long closed at one end with a glass rod. In the space between the tube and rod make a vertical slit ½ in. long with a sharp knife. This acts as a valve which keeps out the air and yet lets out the evolved gases. It is necessary to keep out the air to prevent it from oxidizing any ferrous iron.

Put in the flask 1 gram of Na_2CO_3 and add HCl at such a rate that the liquid will not froth out of the flask. When the carbonate is all dissolved, place the stopper in the flask. Weigh out 1 gram of finely ground ore, transfer to the flask, add a small pinch of carbonate, and then 25 c.c. of strong HCl. Quickly insert the stopper and heat to boiling, and keep at a boiling temperature until the ore is dissolved. Add 200 c.c. of oxygen-free water and titrate with standard dichromate solution. The iron value of the dichromate multiplied by 1.2866 gives the amount of FeO in the ore.

CHAPTER IV

THE DETERMINATION OF PHOSPHORUS IN IRON ORES, IRON AND STEEL

The methods in general use all depend upon first getting the phosphorus into solution, as orthophosphoric acid, and then separating it from the iron and other bases in the form of ammonium phosphodecamolybdate, the so-called "yellow precipitate."

The phosphorus in this is then determined directly or indirectly, and either gravimetrically or volumetrically.

This substance, when dried at 130°C., has uniformly the composition $(NH_4)_3PO_4 12MoO_3$. This formula requires 1.65 per cent. of phosphorus. The average of many most carefully conducted experiments has shown that the precipitate, if free from admixed molybdic acid or other impurities, contains 1.63 per cent. phosphorus within very narrow limits.

The precipitate is only obtained pure when formed under very exact conditions, and is easily affected by subsequent treatment, so that all methods depending upon the weighing of the yellow precipitate or its volumetric determination must be carried out rigorously according to the prescribed directions in every detail.

When a solution of ammonium molybdate in nitric acid is added to an acid solution containing phosphoric acid, the whole of the phosphoric acid is precipitated as the yellow ammonium phosphomolybdate, under the following conditions:

1. All the phosphorus must be present as tribasic (ortho) phosphoric acid.

2. A decided excess of ammonium nitrate or sulfate should be present. The precipitation is most rapid when the solution contains between 5 and 10 per cent. of the salt.

3. A certain excess of free acid must be present—preferably nitric or sulfuric. This must amount to at least 25 molecules of acid for each molecule of P_2O_5 present, and must be increased when sulfates are present.

4. Too great an excess of free acid must be avoided, as this causes decomposition and partial re-solution of the precipitate. This action becomes perceptible when over 80 molecules of acid are present to each molecule of P_2O_5. The concentration of the acid is also important; the smaller the volume of liquid the less free acid must be present.

This solvent action of free acid is prevented by a sufficient excess of molybdic acid solution, which excess must be greater as the amount of free acid is greater. It is also largely overcome by a considerable excess of ammonium nitrate.

5. The yellow precipitate is insoluble in the solution of ammonium molybdate in nitric acid; also in solutions of ammonium salts, if neutral or only very slightly acid, but if strongly acid they attack the precipitate, which is, however, reprecipitated by the addition of molybdic acid solution to the liquid. It is also practically insoluble in a solution of potassium nitrate when neutral and not too dilute. Solutions of salts of organic acids usually dissolve the precipitate to some extent. From these solutions nitric acid and ammonium nitrate, in some cases, reprecipitate the compound, in others, *e.g.*, with tartaric acid or oxalic acid, probably not completely.

The mineral acids, HCl, HNO_3, H_2SO_4, all have a solvent action on the precipitate even in the presence of ammonium nitrate. HNO_3 has the least, HCl probably the most.

Pure water is said to decompose the precipitate to a slight extent and make it run through the filter. This is doubtful, however.

6. Precipitation is much more rapid from hot than from cold solutions but in time it is probably complete at any temperature. The precipitate from hot solutions is denser and more crystalline; from cold, finer and more granular, and harder to filter and wash.

7. Agitation greatly accelerates precipitation in this as well as in other chemical reactions.

8. The precipitate dried to constant weight at ordinary temperatures retains a little acid and water, which it loses when dried at 130°C. By washing the precipitate with a neutral solution of ammonium or potassium nitrate or by prolonged washing with water, it can be freed from acid without drying.

9. Silicic acid in the solution does not seem to interfere with the complete precipitation of phosphorus as yellow precipitate, but a trace of the SiO_2 usually comes down with the precipitate, especially if the solution is too concentrated or too warm, or stands too long. If the solution is rather dilute, not too hot, and is filtered promptly the yellow precipitate can be obtained in the presence of considerable SiO_2 and practically free from it. Titanic acid does not prevent though it greatly delays the precipitation of phosphorus by molybdic acid solution.

10. Organic matter has usually been supposed to interfere with the precipitation of phosphorus, but it is probable that in many cases, noticeably in steel analysis, the bad results attributed to this cause were due to the fact that the phosphorus had not all been converted into the

tribasic acid. The pyro- and meta-phosphoric acids are not completely precipitated by molybdic acid solution.

11. When arsenic acid is present in the solution with the phosphorus, some of it will be precipitated at the same time, the amount increasing with the temperature. Only very small amounts come down at temperatures not exceeding 25°C.

12. MoO_3 may separate with the yellow precipitate as a light crystalline deposit. This free MoO_3 is soluble in acids with difficulty and cannot be washed out of the yellow precipitate. Its separation must always be guarded against when the yellow precipitate is to be weighed or titrated. It forms when the solution contains too much MoO_3, is too concentrated, or too dilute, too strongly acid or too nearly neutral. Too high a temperature precipitates it. The addition of strong nitric acid to a solution of molybdic acid will sometimes precipitate it, as will the adding of molybdic acid solution to solutions of iron in concentrated nitric acid. Long standing favors the separation of excess MoO_3 with the yellow precipitate. A finely divided form of the MoO_3 sometimes separates, easily mistaken for the yellow precipitate and liable to escape notice.

13. Besides the MoO_3, the yellow precipitate may be contaminated by ferric molybdate or ammonium tetramolybdate, which are precipitated by too long digestion or too high temperature. If the precipitate stands at a temperature not exceeding 40°C. contamination in this way is not apt to occur.

14. When the yellow precipitate is thrown down in a solution containing much iron and not sufficient acid, basic iron salts are likely to accompany it, making it reddish in color. This is especially the case when the solutions are hot.

15. The yellow precipitate, if pure, is easily and completely soluble in ammonia (if it contains iron, the solution will be turbid from the formation of ferric phosphate). From this solution the phosphoric acid is completely precipitated by magnesia mixture as $MgNH_4PO_4$. If the yellow precipitate contains any SiO_2, this will also, in part at least, dissolve in the ammonia and separate with the magnesia precipitate, making it a little flocculent. By cautiously adding HCl to the ammonia solution of the yellow precipitate until nearly neutral and letting it stand for some time in a warm place, the silica separates and may be filtered off. The phosphorus may then be precipitated in the filtrate. In precipitating phosphoric acid with magnesia mixture, add the reagent drop by drop and stir the liquid constantly, so that the precipitate separates slowly and in a crystalline form. Otherwise it will be impure, containing magnesia in excess and molybdic anhydride.

The magnesium pyrophosphate must be ignited thoroughly and with access of air to drive off any trace of MoO_3 it may contain.

16. If the sample to be analyzed contains vanadium, the yellow precipitate will be contaminated with it, making the precipitate more soluble. When vanadium is present the precipitate will have an orange color instead of being yellow.

17. Since *complete* precipitation of the phosphorus as *pure* ammonium phosphomolybdate with constant composition is only possible under certain closely controlled conditions, it is necessary for the chemist to find out for himself by repeated experiment exactly what these conditions are, and to standardize his solutions and make his determinations under exactly the same conditions, keeping in mind the many things which may cause error.

To determine the phosphorus, the yellow precipitate may be dried and weighed as such, or it may be ignited to $P_2O_5 24MoO_3$ at a temperature of 450°C. for ten minutes, or the phosphorus may be determined in the yellow precipitate by volumetric methods; thus it may be reduced by nascent hydrogen to $Mo_{12}O_{19}$, which is then oxidized by standard permanganate back to its original condition. Or the yellow precipitate which is an acid anhydride, may be titrated by standard alkali. Lastly the yellow precipitate may be dissolved in ammonia, and the phosphorus precipitated with magnesia mixture and weighed as magnesium pyrophosphate.

For properties of the yellow precipitate and the effects of impurities and associated substances, see

HUNDSHAGEN, *Z. Anal. Chem.*, XXVIII, p. 141; also *Chem. News*, Vol. LX, p. 169.

DROWN, *Trans.* Am. Inst. Mining Eng., XVIII, p. 90.

SHIMER, *Trans.* Am. Inst. Mining Eng., XVII, p. 100.

HAMILTON, *J. Soc. Chem. Ind.*, X, p. 904.

BABBITT, *J. Anal. and App. Chem.*, VI, p. 381.

PATTINSON, *J. Soc. Chem. Ind.*, XIV, p. 443.

MAHON, *J. Am. Chem. Soc.*, 1898, p. 429.

BAXTER, *Am. Chem. J.*, XXVIII, p. 298

On the precipitation by magnesia:

GOOCH, *Am. Chem. J.*, I, p. 391.

FRANK and HINREICHSEN, *Stahl u. Eisen*, XXVIII, p. 295, "Effect of Arsenic."

Note.—According to Chesneau, to get a pure yellow precipitate, the first yellow precipitate should be dissolved in ammonia, then acidified with nitric acid, then after the precipitate comes down, an excess of molybdic acid solution is added, the precipitate allowed to settle,

and then the phosphorus determined gravimetrically or volumetrically. See Rev. Metal., V, 237–69.

Determination of Phosphorus with Final Weighing as Magnesium Pyrophosphate

This method is free from the chances of error due to the presence of impurities in the yellow precipitate. It is gravimetric and the phosphoric acid is finally weighed in a form not subject to variation in composition if care is taken in the precipitation. It is applicable to all kinds of material, and to any percentage of phosphoric acid; hence it is a standard method to which final reference must be made in all important determinations.

Process for Iron Ores.—(In the absence of more than traces of titanium or arsenic.) Weigh 1 to 5 grams, depending upon the percentage of phosphorus, of the very finely pulverized ore. Put it into a 4 in. porcelain dish or casserole, add 1 c.c. nitric acid, then concentrated HCl, using 10 c.c. for each gram of ore taken, and then add 15 c.c. more, cover with a watch-glass, warm until all the iron appears to be in solution, then boil down to dryness, keeping covered to avoid spattering. Dry on a hot plate until the acid is expelled, then add from 30 to 50 c.c. of concentrated HCl, cover and digest until all the iron is dissolved. Now boil down until the volume of the liquid does not exceed 10 or 15 c.c. If the dish is kept covered, there need be no formation of dry salt on the sides. Add water until the volume is 40 or 50 c.c., washing off the cover and sides of the dish. Filter into a 250 c.c. beaker, using a small filter; transfer the residue to a filter and wash until there is no acid taste to the washings.

Dry and ignite the residue. With ordinary ores, if light colored and not too large in amount, it is generally practically free from phosphorus, and may be thrown away. In case the ore is an unknown one, and occasionally even on known ones, the insoluble residue should be fused with sodium carbonate, the fusion dissolved in HCl, evaporated to dryness, and heated to dehydrate the silica. Dissolve the residue in 2 or 3 c.c. of HCl and 10 c.c. of water and filter into the beaker containing the main filtrate.

Instead of proceeding as above, the filtrate from a silica determination may be used for the determination of phosphorus.

The filtrate should not much exceed 100 c.c. To it add 10 c.c. of concentrated HNO_3, and then NH_4OH until a precipitate of $Fe(OH)_3$ is formed which does not disappear on stirring. Now add concentrated HNO_3 until the precipitate just dissolves, then add 3 to 5 c.c. more, which should give to the solution a clear amber color without any red tint. The solution will now be quite warm. Heat if necessary to 80°C. and add from a pipette and with vigorous stirring 50 c.c. of molybdic acid solution. Stir the solution vigorously for several minutes more. Vigorous stirring greatly lessens the time required for precipitation. Allow to stand until the liquid is clear and the precipitate has all settled (this should not require more than one hour): remove a portion of the clear liquid with a pipette and test it by adding a little more molybdic acid solution and warming, to make sure that all the phosphoric acid is precipitated.

Filter the liquid through a 7-cm. filter. Transfer the precipitate to the filter and wash free from iron, with a 1 per cent. solution of ammonium nitrate *very slightly acidified* with HNO_3. The washing must be thorough or difficulty will be experienced when dissolving the precipitate, as phosphates of iron and alumina may form and clog up the filter. When the precipitate is washed, put the beaker in which the precipitation was made under the funnel and redissolve the precipitate on the filter with 20 to 30 c.c. of dilute NH_4OH (about one part of concentrated ammonia to four of water). When it is dissolved and the liquid has all run through, wash the filter three or four times with water, then with a little dilute HCl, to dissolve any ferric or other insoluble phosphate present, and finally with water. Use care in washing, letting each portion of water run through before adding another so as to keep the volume of the filtrate small. This should not exceed 100 c.c. and is usually much less. The filtrate should now be clear and colorless. If it is cloudy or colored (due to a little iron), add HCl until the liquid is acid (the yellow precipitate usually separates), then add four or five drops of a saturated solution of citric acid, then NH_4OH to make the liquid strongly alkaline. This will give a clear liquid, the citric acid holding the iron in solution.

Now add drop by drop a considerable excess of magnesia mixture, stirring the liquid constantly. Estimate the amount from

the probable percentage of phosphorus in the ore taken. Continue to stir the solution vigorously for four or five minutes, then add NH_4OH until the solution smells strongly of ammonia. Let it stand until the precipitate of $MgNH_4PO_4$ has settled completely (one or two hours). The precipitate should be *white and crystalline;* if red or flaky, the results will be inaccurate. Filter on a small filter or better on a Gooch perforated crucible. Wash with water containing one-tenth its volume of concentrated NH_4OH and a little NH_4NO_3, dry, ignite and weigh as $Mg_2P_2O_7$. This contains 0.2787 of phosphorus.

It is essential that the filtrate from the phosphorus precipitate should give at once a strong reaction for magnesium when tested with a drop of a solution of sodium phosphate, as a considerable excess of reagent is necessary to completely precipitate the phosphorus.

Solutions Required. 1. **"Magnesia Mixture."**—Dissolve 22 grams of dry calcined magnesia in as little HCl as possible. When dissolved, add more of the magnesia until some remains undissolved, dilute with several times its volume of water and boil. Any iron oxide, alumina and phosphoric acid will be precipitated. Filter the solution, add 280 grams of NH_4Cl, 800 c.c. of water and 200 c.c. of NH_4OH, sp. gr. 0.90. When all dissolved, dilute to 2000 c.c. Let stand a day or two and decant or filter the solution from any precipitate. Ten cubic centimeters of this reagent will precipitate about 0.07 gram of phosphorus.

2. **"Molybdic Acid Solution."**—Add to 100 grams of molybdic anhydride 300 c.c. of water, and then 120 c.c. of NH_4OH, sp. gr. 0.90. This will dissolve the MoO_3. The solution must smell distinctly of ammonia; if it does not, add more. Unless the solution is clear, filter it, then dilute to about 800 c.c. Now mix 500 c.c. of nitric acid, sp. gr. 1.42, with enough water to make about 1200 c.c. Cool both solutions and mix by pouring the MoO_3 solution into the diluted nitric acid solution, pouring slowly and with stirring. The volume should now be about 2000 c.c. Add to the solution three or four drops of a 10 per cent. sodium phosphate solution, shake thoroughly and allow to settle over night. About once every week or oftener another drop or two of the phosphate solution should be added and the yellow precipitate formed allowed to settle over night. When used, the

clear solution should be pipetted off or filtered. The reason for adding the phosphate solution is as follows: The molybdic acid solution on standing gradually changes with the separation of MoO_3 or ammonia tetramolybdate in too fine a condition to settle. The addition of the phosphate causes the precipitation of ammonium phosphomolybdate, which on settling carries down out of the solution the separated molybdic anhydride, etc.

If the solution of molybdic acid in ammonia is not diluted sufficiently, or if the above directions are not followed as to mixing, molybdic anhydride may separate from the solution as dense curdy precipitate. Forty cubic centimeters of the solution will precipitate about 0.04 gram of phosphorus. Pure MoO_3 must be used in this formula. Some of that on the market is largely ammonium molybdate.

Modification of the Process for Ores Containing Titanium

When ores contain titanium in large amount, the residue will contain considerable iron and phosphorus. The solution of the ore may become turbid on dilution, and the residue run through the filter on washing.

Some of the titanium usually goes into solution and may delay the precipitation of phosphorus. In such cases a larger excess of molybdic acid solution should be used, and a longer time given for the separation of the precipitate.

Process of Analysis.—Weigh out the ore and dissolve it in HCl as in the regular process. If the filtrate from the insoluble residue is not clear add a little HNO_3 and warm, which will probably clear it. If a slight turbidity remains it is of no importance and may be neglected. Now proceed with the filtrate as in the regular process. After the yellow precipitate has been dissolved in ammonia and the filter washed as directed, dry and burn the filter and add the ash to the insoluble residue. This is necessary, as insoluble compounds of phosphorus and titanium may be retained in the filter. This residue is now mixed with eight times its weight of dry Na_2CO_3 and fused as for silica. Boil the fusion with water until thoroughly disintegrated. The phosphorus passes into solution as *phosphate;* while the TiO_2 remains insoluble

as titanate. Filter the liquid from the insoluble matter, acidulate the filtrate with HNO_3 and evaporate to dryness. Add a little HNO_3, then water and filter from the separated SiO_2.

Add to the filtrate 25 c.c. molybdic acid solution and warm, filter off the yellow precipitate and treat it exactly like that from the main solution. Add the phosphorus thus obtained to that obtained from the first solution.

The foregoing treatment is satisfactory for ores with moderate amounts of TiO_2. Where much is present, direct fusion of the ore is advisable.

References:

See a valuable paper by Drown and Shimer, *Trans.* Am. Inst. Mining Eng., X, p. 137. Also Pattinson, *J. Soc. Chem. Ind.*, 1895, p. 443. Discussion, p. 1022.

When ores contain arsenic there is always danger that the final results will be high from the presence of magnesium arsenate.

In this case proceed as follows: To the filtrate from the insoluble residue, which should be in a small Erlenmeyer flask, add a solution of Na_2CO_3 until the liquid becomes dark colored, then add gradually a solution of pure crystallized sodium sulfite (Na_2SO_3) prepared by dissolving the salt in water 1 to 5, and adding HCl until the solution reacts slightly acid. Heat the iron solution to boiling, shaking occasionally. If any precipitate forms, redissolve it with a few drops of HCl. By this time the solution should be *colorless* and all the iron reduced to the ferrous state; if not, continue the warming. When reduced add 10 c.c. HCl, and boil until the odor of SO_2 has gone (usually about three minutes). Remove from the flame and pass a stream of H_2S gas through the liquid for 15 or 20 minutes, or until all the As_2S_3 is precipitated. (The volume of the liquid should not exceed 150 c.c.) The arsenic and any copper present separate completely as *sulfides*. Filter the solution rapidly into a beaker and wash with a little H_2S water. Now boil the filtrate until all the odor of H_2S has disappeared, then add HNO_3 drop by drop to the hot liquid until the change of color shows that the iron is changed to the ferric state. The liquid should become perfectly clear. A faint cloud of separated sulfur may form, but will disappear on heating and does not harm. From this point proceed exactly

as with the filtrate from the insoluble residue in ores when arsenic is not present.

The process depends upon the complete precipitation of arsenic by H_2S in hot strongly acid solutions. The reduction of the iron is necessary to prevent a large separation of sulfur from the action of the H_2S on the $FeCl_3$.

The As_2S_3 precipitate may be used for the determination of arsenic, provided the solution has not been boiled before precipitation by H_2S, which would cause volatilization of $AsCl_3$. See Fresenius Quantitative Analysis for details.

Determination of Phosphorus in Black Band and Other Ores which Contain Much Carbonaceous Matter

These should be weighed out in a porcelain crucible and ignited, taking care not to heat so rapidly as to cause loss by blowing out of fine particles. Set the crucible on its side over a small flame and let the material gradually burn away until all carbon is gone, and an "ash" is left. Treat this by the regular process. Avoid a high temperature in burning or the material will *cake*, thus delaying the combustion and leading to imperfect solution. A dull red heat is sufficient.

Determination of Phosphorus in Mill Cinder

Two points here need attention. First, the material being a soluble silicate, it should be decomposed by weak acid and evaporated to dryness as in the determination of silica after fusion. Second, all mill cinder contains particles of metallic iron, in which phosphorus is present as phosphide. These would evolve PH_3 gas when dissolved in HCl, so HNO_3 must be used to oxidize this phosphorus.

Proceed as follows: Weigh 1 gram into a porcelain dish, add 20 c.c. HNO_3, 1.2 sp. gr., stir well to prevent caking and warm till action ceases, then add 10 c.c. H_2O and 10 c.c. concentrated HCl. Evaporate to dryness and heat on an iron plate to 200°C. for half an hour. Add 10 c.c. HCl, and digest until all the iron is dissolved. Dilute, filter, and proceed as with an ore.

Determination of Phosphorus by the Molybdate-magnesia Process

The phosphorus in iron and steel exists principally as *phosphide*. When these metals are treated with ordinary oxidizing solvents, such as dilute HNO_3, or $KClO_3 + HCl$, the oxidation of the phosphorus is incomplete. Even concentrated HNO_3 fails to convert all the phosphorus into tribasic phosphoric acid. The metal must not be dissolved in HCl or H_2SO_4 as they would cause phosphorus to pass off as phosphine gas (PH_3).

These metals also contain carbon compounds which pass into solution in HNO_3, forming a dark colored substance, and the presence of this dissolved carbonaceous matter is generally supposed to interfere with the precipitation of the yellow precipitate. It seems probable, however, from certain experiments that, if the phosphoric acid is in the tribasic state, this organic matter is without influence. It is certain, however, that unless the oxidizing action is strong enough to destroy this carbonaceous matter completely, the phosphorus is not all oxidized and hence not precipitated completely.

The oldest and most certain method of oxidation is the "dry oxidation method." It consists in dissolving the metal in HNO_3 either concentrated or dilute, sp. gr. 1.2, and then evaporating the solution to dryness. The dry mass of basic ferric nitrate is then heated to about 200°C. for some time. At this temperature the salts are decomposed, the iron largely converted to ferric oxide, and the dissolved carbon and the phosphorus completely oxidized. This residue can then be dissolved in HCl and treated like an ore. The method is always reliable and involves no delicate adjustments.

To save the time required for evaporating the solution and baking the residue, several methods have been devised for oxidizing the material in the nitric acid solution. The reagents most successfully used are potassium permanganate, chromic acid and ammonium persulfate. Aqua regia, potassium chlorate or chlorine fail to oxidize the material completely.

When permanganate is used there is a separation of MnO_2 as a brown precipitate which holds phosphorus and must be entirely redissolved before filtering from the residue or precipitating the phosphorus. This is accomplished by adding a reducing agent, such as oxalic acid, ferrous sulfate, sugar, or potassium nitrite, to the acid liquid. Any considerable excess should be avoided. The MnO_2 is reduced to MnO and dissolved in the acid.

Wet methods are more rapid but are not adapted to all kinds of mate-

rial and must only be used where they have been shown to apply by repeating checking of the results with the standard methods.

When pig-iron or steel, containing silicon, is dissolved in HNO_3, evaporated and "baked," the HCl solution of the residue will be found to filter very slowly because silicic acid in HNO_3 solution is not fully dehydrated on evaporation even if the residue is heated to 200°C. Hence when the residue is treated with HCl some of the SiO_2 goes into the solution and leaves the rest in a highly gelatinous form.

The SiO_2 left after the evaporation of an HCl solution is much more granular and easily filtered off. Therefore, in all cases where silicon is present to any extent the HCl solution of the "baked" residue should be evaporated to hard dryness and again taken up in HCl. This second evaporation takes but little time and is essential, especially with cast-iron, if a long and tedious filtration is to be avoided.

It is stated that the addition of a few drops of HF or a little NH_4F to the first HCl solution will cause it to filter more rapidly and often render the second evaporation unnecessary.

Process for Phosphorus in Iron and Steel.—Take from 1 to 5 grams of the well-mixed borings. Treat them in a covered casserole or dish with 25 to 75 c.c. of HNO_3, sp. gr. 1.2 (made by mixing water and concentrated HNO_3 in equal volumes). Add the acid cautiously to prevent boiling over. Heat until action has ceased and boil down to dryness, using care to prevent spattering, and keeping the dish covered. When dry, set on a hot iron plate and heat the dish to about 200°C. for from 30 minutes to one hour; at the end of this time the material should be hard and scaly and show no trace of acid fumes. Now add from 15 to 25 c.c. concentrated HCl, and digest until the iron is dissolved. Again evaporate to hard dryness and dissolve a second time in concentrated HCl, then proceed as with an iron ore.

Many *steels* will leave no residue insoluble in HCl. In this case filtration as well as the second evaporation is unnecessary.

The phosphorus retained in the residue practically amounts to nothing in the case of irons and steels.

To make the filtration easy, add to the above HCl solution about 50 c.c. water and boil for about 5 minutes. Then let it settle completely, decant off the clear liquid through the filter, and transfer and wash the residue with warm water, adding a little HCl at first. This treatment seems to cause a consolidation of the SiO_2.

Process for Ferrosilicon and Other Difficultly Soluble Alloys

Ferrosilicon with over 10 per cent. of silicon is only slightly attacked by HNO_3 or aqua regia. This and other insoluble alloys cannot be treated by the foregoing method for the determination of phosphorus. With ferrosilicon, if the percentage of silicon is not too high, the addition of a little HF or NaF to the HNO_3 and metal in the dish will cause it to dissolve and then the regular method can be followed. About as much NaF should be added as there is silicon present. The metal should be very finely pulverized; this presents no difficulty as these alloys are all brittle. The metal should be crushed in a steel mortar until it will all go through a 100-mesh sieve and then the portion to be used in the analysis rubbed down in an agate mortar.

Samples not attacked by the fluoride must be fused. Mix the very finely ground sample with five or six times its weight of a fusion mixture of equal parts of Na_2CO_3 and $NaNO_3$ and fuse in a platinum crucible. Apply the heat cautiously until the first reaction is over and the mass is quiet, then raise the temperature till fusion is complete. Avoid using a higher temperature than is necessary as the platinum is likely to be attacked. The fusion can then be taken up in water and HCl and the phosphorus determined as usual.

HCl must not be added in the crucible as chlorine may be formed and attack it, but after the mass has been soaked out with water any adhering Fe_2O_3 may be dissolved in a little HCl.

Instead of dissolving the whole fusion in HCl, it may be boiled with water, the lumps being crushed fine, and the solution then filtered from the Fe_2O_3 and acidified; the filtrate will contain all the phosphorus as sodium phosphate with some silicate. The residue should be tested, however, in important cases. A blank must be run on the reagents.

Sodium peroxide is sometimes used instead of the nitrate; it works rapidly and is a powerful oxidizing agent, but is not so easy to obtain pure. It acts at so low a temperature that nickel crucibles can be used in the fusions and the wear on the platinum saved. These fusions are very destructive to platinum, which should not be used when the metal is fused with sodium peroxide alone.

In fusing ferrosilicon with sodium peroxide alone a large excess of the

reagent must be used or the reaction becomes very violent; at least eight parts of peroxide to one of metal are required. The temperature of fusion need not exceed a dull red.

Determination of Phosphorus by Weighing the Yellow Precipitate

This method is generally used as a "rapid method." It is not, however, as rapid as the volumetric method for phosphorus, but it is the most rapid of the gravimetric methods.

Since accurate results by this method depend upon purity of the yellow precipitate, and uniform composition of the same, it is necessary that the conditions of precipitation be strictly controlled and that the process be checked by running the phosphorus in a standard sample under exactly the same conditions as obtain in the routine work of the laboratory.

The yellow precipitate is quite hygroscopic, hence it must be weighed promptly and with the least possible exposure to the air.

As the yellow precipitate has 1.63 per cent. of phosphorus it is convenient to take that amount in grams for analysis. The drying and weighing of more than 0.4 gram of yellow precipitate is difficult, hence for ores having over 0.4 per cent. of phosphorus, take one-half of the above amount (0.815).

Process for Iron Ores.—Weigh 1.63 grams of the finely pulverized ore into a 4-in. casserole, add 25 c.c. concentrated HCl, digest, evaporate to dryness and heat as in the former process. Now add 20 c.c. HCl, and digest until all the iron is dissolved. Add 30 c.c. of water, boil, let settle and filter into a beaker of 250 c.c. capacity; wash with small portions of water several times. The volume of the filtrate need not exceed 70 or 80 c.c. Now add 35 c.c. of strong nitric acid and boil down rapidly until the volume of the liquid is 15 c.c. Take from the hot plate, wash off the cover and dilute to 50 c.c. Add NH_4OH until a permanent precipitate forms, then add nitric acid until the precipitate just dissolves, then 3 c.c. more. Heat to 80°C., add 50 c.c. of molybdic acid solution slowly and with stirring and continue the stirring for several minutes. The precipitate should settle out perfectly clear in one-half hour.

Fold a 4-cm. filter, put in the air-bath and dry at 110°C. for 15 minutes. Place it quickly between two watch-glasses which

fit tightly, and weigh immediately. The weights for the watch-glasses should already be on the balance pan before the paper is weighed. Weigh to the nearest milligram.

Place the paper in a small funnel, filter and transfer the precipitate to it. Wash out the beaker and wash the precipitate five times with a solution of molybdic acid (1 part molybdic acid solution to 3 parts water). Finally wash the precipitate at least six times with 2 per cent. HNO_3 solution. Set the funnel and contents in an air-bath and dry at 110° for 30 minutes after all visible moisture has disappeared. Quickly place the paper between the watch-glasses and weigh. The difference in weight between the first and second weighings gives the yellow precipitate and this in grams gives the percentage of phosphorus.

Instead of weighing the yellow precipitate as such, the following process may be used: Place the funnel with the precipitate in it above a weighed platinum crucible and wash the precipitate with hot NH_4OH until it is entirely in the crucible. Evaporate the solution in the crucible to dryness, then heat to 400–450°C. in an air-bath. Do not heat to a red heat as some MoO_3 will volatilize. Ten minutes' heating is enough. The factor for phosphorus in the $P_2O_5 24MoO_3$ thus obtained is 0.0169; that is, the residue contains 1.69 per cent. phosphorus.

Process for Iron and Steel.—Weigh 1.63 grams of the well-mixed borings into a 4-in. casserole. Add cautiously 35 c.c. HNO_3, sp. gr. 1.2, boil to dryness, then bake for 30 minutes on a hot plate at 200°C. Dissolve in 20 c.c. HCl and if silicon is present again evaporate to dryness and dissolve a second time. Now proceed as in the case of ores, except that if the steel dissolves without residue filtration is unnecessary.

The above methods assume that the phosphorus all passes into solution and that arsenic is absent. Titaniferous and arsenical ores and metals must be treated by the first method.

The yellow precipitate method as described, may be much shortened for steel and pig-iron by using wet methods of oxidation. For the use of permanganate for oxidizing the phosphorus, see Volumetric Method for Phosphorus on page 49.

The Chromic Acid Method is as follows: Dissolve 1.63 grams of steel in 30 c.c. of nitric acid, sp. gr. 1.20, in a 175 c.c. Erlenmeyer flask. Place the flask over a burner and evaporate to

15 c.c. Add to the boiling solution 20 c.c. of a solution of 30 grams of CrO_3 in 2000 c.c. of HNO_3, sp. gr. 1.42. Dissolve the chromic acid by heating. The solution will keep only about two weeks.

Evaporate the contents of the flask to 18 c.c. Wash down with 7 c.c. of water, cool to 45°C., and add 60 c.c. of clear molybdic acid solution previously heated to about 40°C. Shake well for five minutes, let settle for 15 minutes, filter, wash and weigh.

Volumetric Methods for Phosphorus

These are based on the precipitation of the phosphorus as phosphomolybdate and determination of the amount of the precipitate by estimating the molybdic acid contained in it volumetrically, either by reduction with zinc and titration with potassium permanganate, or by neutralizing it with standard alkali.

Emmerton's Method. Titration by Permanganate.—When the yellow precipitate is dissolved in NH_4OH and mixed with a very considerable excess of H_2SO_4, it all remains in solution. If this solution is warmed with metallic zinc, zinc dissolves, and the molybdic acid is rapidly reduced, giving first a dark red and finally a green solution containing, if the reduction is complete, Mo_2O_3. If this solution is rapidly filtered from any undissolved zinc, it can be titrated with a solution of potassium permanganate which promptly oxidizes the Mo_2O_3 back to MoO_3. The solution becomes colorless and finally when oxidation is complete is colored pink by the least excess of permanganate.

The color of the reduced solution depends somewhat upon the excess of sulfuric acid present. If this is too large the green color will not be reached and the end of the reduction cannot be determined. The smaller the excess of H_2SO_4 the sharper is the change from red to green at the end.

Complete reduction is a matter of considerable difficulty and the methods in use do not always attain it. This has given rise to the assigning of various formulas to the reduced product. Emmerton gives $Mo_{12}O_{19}$, which probably most nearly represents the usual product of the reduction method he describes. The reductor gives ratios between the molybdenum and the oxygen which vary with the methods of using it. Blair and Whitfield give for the reductor product $Mo_{24}O_{37}$.

References:

Emmerton, *Trans.* Am. Inst. Mining Eng., XV, p. 93.

Dudley and Pease, *J. Am. Chem. Soc.*, 1894, p. 224.

W. A. Noyes, *J. Am. Chem. Soc.*, 1894, p. 553.
W. A. Noyes, *J. Am. Chem. Soc.*, 1895, p. 129.
Blair and Whitfield, *J. Am. Chem. Soc.*, 1895, p. 747.
Auchy, *J. Am. Chem. Soc.*, 1896, p. 955.

This uncertainty as to the reduction product makes the standard permanganate solution of uncertain value in phosphorus if standardized against metallic iron only; hence, it is better to check it against a standard steel, ore or pig-iron, of known phosphorus content which should be treated exactly by the method used in the regular analysis.

The widely extended use of this method shows, however, that although there is some uncertainty as to the nature of the oxide produced by reduction, this possibly being different for different workers, by working always in exactly the same way, the reduction is uniform, and hence the titration is a reliable method for estimating the yellow precipitate, and indirectly the amount of phosphorus.

Preparation of the Solution of Potassium Permanganate.—To compute the strength of this solution assume that the reduction of the yellow precipitate gives $Mo_{12}O_{19}$. Then the permanganate solution must furnish 17 atoms of oxygen for each 12 molecules of MoO_3 present before reduction to oxidize the $Mo_{12}O_{19}$ back to MoO_3. The yellow precipitate contains 24 MoO_3 to 1 of P_2O_5 or 12 of MoO_3 to 1 of P; hence the permanganate must furnish 17 atoms of oxygen for every atom of phosphorus present in the precipitate.

The permanganate used may be either the one used for titrating iron or one made especially for phosphorus determinations. In the former case, the value of the permanganate in terms of phosphorus is obtained as follows: One atom of oxygen can oxidize two atoms of ferrous iron to ferric iron; hence the reducing power of the reduced yellow precipitate is equal to 17×2 or 34 atoms of ferrous iron. Therefore,

One atom of P. : 34 atoms of Fe : : X : Fe value of the permanganate, or 31 : 1898.9 : : X : Fe value of the permanganate. Solving for X we find that the iron value of the permanganate multiplied by 0.01634 equals the phosphorus value of the permanganate.

To make a solution of such strength that 1 c.c. equals 0.01 per cent. of phosphorus on a 1 gram sample, note that two molecules of permanganate will yield oxygen thus: $2KMnO_4+3H_2SO_4 = K_2SO_4+2MnSO_4+3H_2O+5O$. That is, two molecules of per-

manganate will give up five atoms of oxygen. Therefore to yield 17 atoms of oxygen which is the amount required to oxidize one molecule of the reduced yellow precipitate (equivalent to one atom of phosphorus) requires $17 \times \frac{2}{5}$ or $6\frac{4}{5}$ molecules of $KMnO_4$. Therefore:

$$6\frac{4}{5}KMnO_4 : 1P. :: X : 0.0001,$$

or 1074.6 : 31.04 : : X : 0.0001. X equals 0.003462 gram $KMnO_4$ per c.c. or 3.462 gram per liter.

To make the solution, heat 1 liter of water to boiling and add dilute $KMnO_4$ until a faint pink appears. Cool to room temperature and dissolve 3.462 grams of pure permanganate in 500 c.c., then dilute to a liter.

To standardize, dissolve 0.8589 gram $(NH_4)_2SO_4.FeSO_4.6H_2O$. in 200 c.c. of water and 5 c.c. H_2SO_4 and titrate to a faint pink. This amount of iron salt contains 0.1224 gram of iron, which is equivalent to $0.1224 \times 0.01634 = 0.002$ gram of phosphorus; therefore 20 c.c. of the solution should be required. If more or less is taken, calculate the amount of phosphorus to which 1 c.c. is equivalent by the proportion, $n : 20 = 0.0001 : x$, n being the amount used and x the value sought.

The determination of the value against a known steel is desirable, as it gives a result which is independent of all assumptions as to the nature of the oxide produced by the zinc reduction. The permanganate solution should be kept in a dark bottle carefully protected from dust and other organic matter, and used only in burettes with glass stop-cocks.

Process for Iron or Steel.—Weigh 3 grams of steel or 1 to 3 grams of iron, according to the percentage of phosphorus, into a 4-in. casserole, and add 25 to 75 c.c. of HNO_3, sp. gr. 1.2. Add the acid cautiously to avoid boiling over. After action has ceased, cover and boil down to dryness, then bake on a hot plate 30 minutes and add 20 to 40 c.c. concentrated HCl. Heat until all the iron oxide is dissolved.

If the metal contains much more than a trace of silicon, evaporate the solution to dryness and dissolve again in the same amount of HCl. Finally, boil down to 15 c.c., being careful to avoid the formation of any dry crusts on the sides of the dish. This is accomplished by keeping the dish well covered and shaking it around a little.

Now add 20 to 40 c.c. concentrated HNO_3, using the acid to wash the cover. Boil down again to 10 or 15 c.c. It is essential that no dry iron salt form on the sides. This is easily avoided by covering with an inverted watch-glass a little smaller than the dish, so that the condensed acid will flow down the sides and keep them clean. Cool slightly, moving the liquid around so as to dissolve any crusts of ferric nitrate formed. Now add 30 to 50 c.c. of water and filter into a 400 c.c. Erlenmeyer flask. The volume should be about 75 c.c. Steels do not require filtration, as a rule, for they leave no residue if low in silicon.

Now add NH_4OH until the ferric hydroxide separates and the mass becomes thick and smells of ammonia. Then add strong HNO_3 gradually until the precipitate redissolves and the liquid has a clear, *amber* color, not the least red. The volume should now be about 150 c.c.; if not, dilute to that amount. Then put a thermometer in the liquid and bring the temperature to 80°C. Now add at once 40 c.c. of molybdic acid solution. Close the flask with a rubber stopper, wrap it in a thick cloth and shake violently for five minutes.

This violent agitation, combined with the high temperature, causes the yellow precipitate to separate promptly and in a particularly dense and easily filtered form.

Finally, let settle for a few moments, and filter off the solution, using a 9-cm. filter. Wash the flask and precipitate several times with a solution made by diluting the molybdic acid solution with five times its volume of water. Finally, wash well both flask and precipitate with pure water until the washings do not react acid. Now set the funnel in the flask and dissolve the precipitate back into it with dilute NH_4OH (1 : 4) using altogether 30 c.c. To save time some chemists puncture the filter and wash the precipitate through with water. Wash the filter, using as little water as possible.

Finally wash the filter again with NH_4OH then with water. Now add 80 c.c. of dilute H_2SO_4 (one volume to four of water) to the filtrate and then 10 grams of pulverized zinc.

The zinc should be fine enough to pass a 20-mesh sieve and must be as free as possible from iron. The very pure zinc now furnished for this process will sometimes act very slowly. To make it act promptly it should first be platinized as follows:

Treat a quantity of the zinc with water, slightly acidulated with H_2SO_4 and containing a few drops of a solution of $PtCl_4$. After the reaction has proceeded a few minutes, pour off the liquid and wash the zinc thoroughly with water; dry it and preserve it in a glass-stoppered bottle. The almost infinitesimal trace of platinum precipitated on the zinc by this treatment causes the reaction to be rapid and powerfully reducing on the MoO_3.

Now warm till rapid effervescence ensues and heat gently 10 *minutes*. At the end of this time reduction will be complete. Meanwhile, fold a 12-cm. filter in "ribs," put it in a funnel, and as soon as the reduction of the MoO_3 is complete pour the liquid off from the residue of the zinc into the filter, collecting the filtrate in a white dish. Rinse the flask and zinc once with water and pour this on the filter after the solution has run through. Then fill the filter with water and let it run through. Thin filter paper must be used so that the whole operation of filtration and washing the zinc shall occupy but three or four minutes.

Instead of filter paper absorbent cotton may be used, a small plug being placed loosely in the neck of the funnel. This should be moistened and the solution poured directly on to it. This will filter very rapidly and satisfactorily.

Now run the permanganate into the dark colored filtrate till the color is discharged, and the last drop gives a faint pink tint, marking the end of the reaction.

There is always some impurity in the zinc, hence it is essential to make a *blank test*, using the 30 c.c. of NH_4OH, the 10 grams of zinc and 80 c.c. of sulfuric acid as before, but omitting the yellow precipitate. The filtrate in this test will always consume a small amount of permanganate, which must be determined, and deducted from the amount taken in the regular determination, the difference being the permanganate solution equivalent to the yellow precipitate.

The number of cubic centimeters of permanganate solution used, after correction for error of standard, divided by the number of grams of metal taken will give the amount of phosphorus in hundredths of 1 per cent.

In working this process it is important to check it from time to time upon material similar to that to be analyzed, and in which the phosphorus has been determined gravimetrically.

The Emmerton Method with Wet Oxidation

By substituting wet methods of oxidation for the baking in the regular process and using the reductor for reducing the molybdic acid, the Emmerton method becomes extremely rapid. It then depends upon such nice adjustment of conditions, however, that it should be especially tested for any variation in the material treated. The permanganate in these processes should be standardized against a steel of approximately the same phosphorus content as that to be analyzed. This is desirable not only on account of the uncertainty in the reduction product but also on account of the fact that the completeness of precipitation of the phosphorus by the molybdic acid solution depends somewhat on the treatment and also upon the percentage of phosphorus in the steel. For example, if a steel containing only 0.04 per cent. of phosphorus were used to standardize the permanganate and the method of precipitation left 0.001 per cent. of phosphorus in the solution it is obvious that while the permanganate so standardized would give satisfactory results on another steel of about the same phosphorus content it would give entirely false results on a steel containing several times as much phosphorus, as the ratio between the phosphorus remaining in solution and that precipitated would be entirely different. Any change in the routine of the precipitation of the phosphorus will also obviously require a re-standardization of the permanganate.

By using nitric acid of sp. gr. 1.13 as a solvent the separation of SiO_2 is prevented and filtration is rendered unnecessary.

Process for Steels.—Dissolve 2 grams of the well-mixed drillings placed in a 300 c.c. Erlenmeyer flask in 70 c.c. of HNO_3 sp. gr. 1.13 (made by mixing 4 parts of concentrated HNO_3 and 9 parts of water). Heat to boiling to expel most of the nitric oxide, then add in two or three portions 8 to 10 c.c. of a solution of $KMnO_4$, 12 grams to the liter. Boil till the pink color disappears, then add a solution of $NaNO_2$ drop by drop till the brown precipitate of MnO_2 is redissolved and the solution becomes clear.

Add NH_4OH to neutralize the greater part of the free HNO_3 which will be the case when the amber color disappears and to solution grows red; then add sufficient HNO_3 to bring back the amber color. Dilute to 150 c.c., heat to 80°C. and add 50 c.c. of molybdic acid solution. Agitate for five minutes by shaking or by blowing a current of air through the solution. Allow to

stand for two or three minutes or longer, if necessary to settle the precipitate, and filter, washing as in the preceding process. Set the funnel in the flask in which the precipitate was made and dissolve the precipitate on the filter in NH_4OH (1 : 4) using altogether 20 c.c.; then wash the filter well with water. Add 50 c.c. of H_2SO_4 (1 : 4), dilute to 150–200 c.c. and reduce either by adding 10 grams of pulverized zinc and heating for 10 minutes as in the Emmerton method, or by passing the dilute solution (200 c.c.,) through the zinc reductor as described in the iron assay.

Titrate the reduced solution with $KMnO_4$ till a faint pink remains, not disappearing within a minute. Calculate the percentage of phosphorus from the strength of the $KMnO_4$ solution and the number of cubic centimeters used.

After having made a few analyses and having determined the proper amount of NH_4OH necessary to add in neutralizing the excess of HNO_3, time may be saved by adding this amount at once, and avoiding the working back with HNO_3. The solution is then shaken till the precipitate redissolves, diluted to 150 c.c., cooled or warmed to 80° and the phosphorus precipitated by molybdic acid solution.

This addition of the proper amount of NH_4OH is not only quicker but gives more satisfactory results than by determining the proper acidity of the solution each time by the depth of the amber color, since this color varies with the sample of steel, the amount of sample taken, and the volume and temperature of the solution.

The yellow precipitate must be washed free from iron salts or the results will be incorrect, since the iron if washed into the flask with the precipitate will dissolve in the acid and be reduced with zinc and titrated with permanganate.

Titration of the Yellow Precipitate with Standard Alkali

This method is in the writer's opinion the best for steels or samples low in phosphorus. It is both rapid and accurate. It avoids the reduction and consequent uncertainty as to the oxide produced. The reaction may be written as follows:

$$12MoO_3,\ (NH_4)_3PO_4 + 23NaOH = 11Na_2MoO_4 + (NH_4)_2MoO_4 + Na(NH_4)HPO_4 + 11H_2O.$$

Hundeshagen has shown that 23 molecules of NaOH are required to neutralize 1 molecule of yellow precipitate. This gives a ratio of 1 atom of phosphorus to 23 molecules of NaOH or by weight 31 of P to 921.15 of NaOH, or 1 : 29.71. The alkali solution must be free from carbonate which would interfere with the end reaction. The best indicator is a dilute alcoholic solution of phenolphthalein. The alkali solution should be standardized on pure yellow precipitate carefully dried to constant weight at 150°C. As this substance is rather hygroscopic, it should be redried every time it is used.

To prepare the yellow precipitate for standardizing, precipitate a dilute solution of Na_2HPO_4 by an excess of molybdic acid solution, first acidifying the phosphate solution with HNO_3. Wash the precipitate carefully with water and dry it as directed. Determine the phosphorus in a portion of it gravimetrically. It should contain 1.63 per cent. of phosphorus.

Preparation of the Solutions. Standard Sodium Hydroxide and Standard Nitric Acid.—One-tenth normal solutions may be used. In this case 1 c.c. NaOH is equal to 0.000135 gram phosphorus.

It is more convenient to have a solution of such a strength that 1 c.c. equals 0.0002 gram phosphorus; then if 2 grams of steel are taken for the analysis, each cubic centimeter of hydroxide solution will be equivalent to 0.01 per cent. of phosphorus. To make such a solution, proceed as follows:

Dissolve 15.4 grams of NaOH as free as possible from Na_2CO_3 in about 200 c.c. of water. Now add a saturated solution of $Ba(OH)_2$ as long as a precipitate forms. Filter at once from the $BaCO_3$ and dilute to 2 liters. This solution will be a little too strong. Now prepare an approximate HNO_3 solution by diluting 20 c.c. of concentrated HNO_3 to 2 liters. Fill a burette with this acid and titrate it carefully against 10 c.c. of the NaOH solution. Next weigh 0.1226 gram of dry yellow precipitate (equal to 0.002 gram of P) into a beaker; add 50 c.c. of water and 10 c.c. of the NaOH solution which should dissolve the precipitate to a perfectly clear solution. Now add 3 drops of phenolphthalein solution and titrate with the acid till the color vanishes. The difference between the acid required for the NaOH and that required in the second case is the number of cubic centimeters of the HNO_3 equivalent to 0.002 gram phosphorus. Now add sufficient water to the dilute nitric acid to make 10 c.c. exactly

equal to 0.002 gram phosphorus. Repeat the test with the yellow precipitate and soda solution, using double the amount of yellow precipitate and 30 c.c. of soda. If the nitric acid is not exactly right, correct it by further dilution and repeat the test. Finally dilute the soda solution until it is exactly equivalent to the nitric acid.

As a check the HNO_3 should also be standardized against pure sodium carbonate (Na_2CO_3). Proceed as follows: Put 5 grams of the pure salt in a platinum crucible, cover the crucible with a lid and embed the crucible nearly to the top in a sand bath and place a thermometer in the sand by the side of the crucible. Heat the sand bath until the temperature rises to 270–300°C., and keep it at that temperature for a half hour. This is to drive out all moisture without decomposing the carbonate. Cool the crucible and contents in a desiccator. Weigh out 0.265 gram of the carbonate, dissolve in 20 c.c. of distilled water, add a few drops of methyl orange indicator and titrate with the nitric acid solution until its color becomes distinctly red when compared with the color of another solution of the same volume containing the same amount of methyl orange and a little sodium carbonate. If the nitric acid is exactly N/10, just 50 c.c. should be required for the titration.

The nitric acid, if preserved in a tightly stoppered bottle, keeps its standard indefinitely, but the soda solution will slowly change on account of absorption of CO_2 by the slight excess of $Ba(OH)_2$ present and must be retested against the acid frequently. This can be prevented by using a guard tube containing soda-lime. The soda solution also changes strength by attacking the glass. This is avoided by paraffining the inside of the bottle.

In standardizing the acid and alkali, instead of taking yellow precipitate directly a sample of steel of known phosphorus content may be weighed out and treated as in the regular process. It is well to finally check the solution in this way in all cases.

Phenolphthalein Solution.—Dissolve 0.2 gram of the indicator in 200 c.c. of 95 per cent. alcohol.

Methyl Orange Solution.—Dissolve 0.025 gram of the sodium salt in 100 c.c. of water and add 0.70 c.c. of N/10 HCl.

Process for Steel.—Weigh out 2 grams of the well-mixed drillings into a 400 c.c. Erlenmeyer flask. Add 70 c.c. HNO_3,

sp. gr. 1.13. Heat till the metal is dissolved, then add to the boiling solution 7 to 8 c.c. of a solution of $KMnO_4$, 12 grams to the liter. Boil till the pink color disappears and a precipitate of MnO_2 forms. Then add a little pure ferrous sulfate, sodium nitrite or tartaric acid, and heat till the solution clears. Remove from the burner, add NH_4OH until the amber color of the solution darkens distinctly and takes a reddish tint. Then add enough HNO_3 to restore the amber color to the solution. Dilute to 150 c.c. and cool or warm to 80°C. Add 50 c.c. of molybdate solution and shake five minutes. Filter, and wash the flask and the precipitate several times with dilute MoO_3 solution, then with 1 per cent. KNO_2 solution till neutral. Put the filter containing the precipitate back into the flask in which the precipitation was made, and add to the flask and its contents a measured quantity, usually 10 or 20 c.c. of standard NaOH. Dilute to 50 c.c. with CO_2 free water, add 2 drops of phenolphthalein; shake to disintegrate the filter and dissolve the precipitate, and then titrate the excess of alkali with standard acid. The difference between the number of cubic centimeters of nitric acid equivalent to the soda solution used and that required in the titration will be the nitric acid equivalent to the phosphorus; and if the nitric acid is of correct strength each cubic centimeter will represent 0.01 per cent. of phosphorus.

When this method is applied to pig-iron it is best to add a gram of ammonium persulfate to the solution when the iron is all dissolved and then boil to destroy the combined carbon. Then filter off the residue and add permanganate to the filtrate and proceed as above.

The process may be somewhat shortened, as noted before in the Emmerton process, by determining the amount of NH_4OH required to neutralize the excess of acid and adding it at once, thus avoiding the reacidifying with HNO_3. This amount can be easily ascertained after a few trials, noting the amount of NH_4OH used, the amount of HNO_3 required to bring it back, and then determining by trial how much NH_4OH is needed to neutralize the amount of acid so used and deducting it from what was originally added.

In dissolving yellow precipitate by standard alkali always keep the liquid cool and the solutions dilute, as ammonia is set free

in the reaction and is liable to be lost by volatilization if the liquid is concentrated. This would cause error in the nitric acid titration.

References on the Titration Method:
J. Anal. and App. Chem., VI, p. 82.
J. Anal. and App. Chem., VI, p. 204.
J. Anal. and App. Chem., VI, p. 242.
Z. Anal. Chem., XXVIII, p. 171.
Stahl u. Eisen, XXVI, p. 297.

The Determination of Phosphorus in Steel Containing Vanadium

The presence of vanadium in steel interferes with the determination of phosphorus by making the precipitation with the molybdic acid incomplete and the precipitate impure with vanadium. The following method of E. W. Hagmaier[1] is short and accurate.

Process of Analysis.—The sample of steel is dissolved in aqua regia, evaporated to dryness and baked. When all the acid is driven off it is then taken up in strong hydrochloric acid; when complete solution is obtained the silica is filtered. The filtrate is then reduced with sulphurous acid. When entirely reduced 5 c.c. of acetic acid 90 per cent. and 10 c.c. of saturated cerium chloride solution are added. NH_4OH (about 1 part concentrated ammonia to 3 of water) is added drop by drop with constant stirring, until turbidity is shown. The solution is then heated to boiling, allowed to settle, and filtered. The cerium phosphate will filter rapidly, especially through a black ribbon paper. The precipitate is washed five or six times with hot water and then dissolved off the paper with hot (1–1) nitric acid, and the phosphorus precipitated as in other cases with ammonium molybdate.

Notes on the Method.—It is better to filter off the silica before precipitating the cerium phosphate, for the presence of the silicon causes the cerium phosphate to filter slowly.

The point where most caution is required in the whole method is in adding the NH_4OH. This must be added very slowly, for if too large

[1] E. W. Hagmaier, *Met. Chem. Eng.*, XI, p. 28.

an amount is once added it seems impossible to obtain proper conditions by coming back again with hydrochloric acid. If by accident too much NH_4OH is added, the best plan is to filter the precipitate, redissolve it in hydrochloric acid, pass in sulfur dioxide, and reprecipitate the cerium phosphate.

This method has been tried with vanadium from 0.166 up to 5 per cent. and it has been found that in all cases above 0.5 to 1 per cent. one reprecipitation of the cerium phosphate should be made, and with 1 per cent. to 5 per cent. vanadium two reprecipitations.

Determination of Phosphorus by Measuring the Volume of the Yellow Precipitate.—This method is occasionally used for furnace control in steel plants. It requires a special centrifugal machine and graduated bulbs with small collecting tubes for the precipitate. A description will be found in the Journal of Analytical and Applied Chemistry, Volume IV, page 13.

With practice it is possible to estimate small percentages of phosphorus in steel by judging the amount of the yellow precipitate as it collects on the bottom of the ordinary precipitation flask. Such estimation will usually serve the same end as is accomplished by the centrifugal apparatus.

The Determination of Phosphorus in Ferro-alloys

The determination of phosphorus in these samples calls for special treatment. Most of the ferro-alloys are very difficultly soluble in acids, and fusion must be resorted to to effect decomposition.

Process for Ferrotitanium and Ferrochrome.—Place in a platinum crucible 20 grams of sodium carbonate thoroughly mixed with 4 grams of potassium nitrate. Then mix in 1 gram of the powdered sample and heat to fusion. When the melt is in a state of quiet fusion, keep it at a bright heat for 30 minutes longer. Allow to cool, transfer the cake to a 4-in. casserole and dissolve in hot water. If any titanium is present, it remains insoluble as sodium titanate. Chromium, sulfur, phosphorus, silicon, and manganese go into solution as sodium chromate, sulfate, silicate, and manganate. Filter and wash thoroughly with a hot dilute sodium carbonate solution. The iron stays on the filter as ferric oxide with the sodium titanate. To the solution add 1:1 HCl until it is slightly acid. Add a solution of ferric chloride con-

taining 0.05 gram of iron, add NH_4OH until the solution is just alkaline, then acidulate slightly with acetic acid. Boil for a few minutes, filter and wash the precipitate of ferric phosphate and hydroxide with hot water. Dissolve the precipitate on the filter in hot dilute HCl, evaporate the solution to dryness, redissolve in a few drops of HCl, dilute to 70 c.c., filter if there is any silica present, add 5 c.c. of HNO_3, then NH_4OH until just alkaline. Now add 3 c.c. of HNO_3, heat to 80°, add molybdic acid solution and determine the phosphorus as usual.

Phosphorus in Ferrotungsten.—Johnson has shown that the method of decomposing high tungsten materials by fusion with sodium carbonate and niter and leaching out the fusion with water, with subsequent separation of the tungsten by evaporation to dryness with HCl gives low results. He gives the following method as being fairly correct.

Process of Analysis.—Dissolve 1 gram of sample in a platinum dish with 30 c.c. of HNO_3 and 3 c.c. of HF. The sample should dissolve to a clear solution after heating to boiling. Transfer to a porcelain dish and evaporate to dryness, but do not bake. Dissolve the residue in 50 c.c. of HCl, sp. gr. 1.2, and again evaporate to dryness, without baking. Dissolve the residue in 20 c.c. of HCl, heat, add 50 c.c. of water, heat and filter, and wash with dilute HCl. Evaporate to 10 c.c., add 20 c.c. of water, filter and wash. Evaporate to 10 c.c., add 75 c.c. of concentrated HNO_3, heat until all action is over and evaporate to 20 c.c. Add 50 c.c. HNO_3 and again evaporate to 10 c.c. Add 20 c.c. of water, heat and filter and wash with 2 per cent. HNO_3. To the filtrate add a slight excess of $KMnO_4$ and carry on the determination of the phosphorus as in a steel.

Reference:
Johnson, *J. Ind. Eng. Chem.*, V, 297.

Process for Ferrosilicon and Ferro-manganese.—Fuse as for ferrotitanium, dissolve in a casserole in hot water, then add HCl, keeping the casserole covered with a watch-glass, until an excess of acid has been added and everything is in solution. Wash off the cover and evaporate to dryness on a water-bath. Add 10 c.c. of strong HCl, heat until the iron all goes in solution, dilute and filter. Now add ferric chloride to the solution, and proceed as above.

Process for Ferrovanadium.—As has been mentioned before, vanadium precipitates with the yellow precipitate and furthermore prevents the complete precipitation of the phosphorus, so the vanadium must be separated from the phosphorus. The following method is due to C. M. Johnson (See Chemical Analysis of Special Steels and Steel-making Alloys and Graphites, page 21). Fuse 1 gram of sample as directed above for ferrotitanium. Proceed until the residue is obtained on the filter paper; burn this in a platinum crucible and make a second fusion and extraction. The combined filtrates and washings are placed in a large beaker and 5 c.c. of sodium aluminate solution is added. (Sodium aluminate is made by placing 10 grams of metallic aluminium in a large dish with 50 grams of caustic soda. Water is added very carefully until the reaction is complete. The mass of aluminate is dissolved in water, filtered, and diluted to 500 c.c.).

HCl 1 : 1 is added until the solution no longer changes turmeric paper at once to even a faint brown.

Aluminium hydroxide and phosphate precipitate. The precipitate is filtered and washed with ammonium nitrate solution, roasted in a platinum crucible and again fused with 10 grams of sodium carbonate and 2 grams of potassium nitrate. The melt is dissolved in water, filtered and precipitated again with 1 : 1 HCl. This precipitate is then washed, dissolved in 5 c.c. of HNO_3, diluted to 75 c.c., NH_4OH added until alkaline, nitric acid added and the phosphorus precipitated and estimated as usual.

Determination of Phosphorus in Tungsten Steel.—Dissolve the sample in a mixture of 30 c.c. of HNO_3 and 30 c.c. of HCl. Heat until action ceases and the residue in the bottom of the dish is bright yellow. If it is not, repeat the addition of acid. Now evaporate to a small volume, add 50 c.c. more HNO_3, and evaporate to hard dryness, finally heating nearly to a red heat. Cool, add 50 c.c. of strong HCl, and heat until the residue is a bright yellow and no iron is left undissolved. The residue is WO_3, SiO_2, with small amounts of iron and chromium. Filter, wash, and evaporate to a small volume, add a little water and filter to remove what little WO_3 may be present. In the filtrate determine the phosphorus, as in the case of any steel.

CHAPTER V

THE DETERMINATION OF SILICON IN IRON

The metals in which silicon has most frequently to be determined are pig-iron, containing from ½ to 4 or 5 per cent.; "ferrosilicon," containing up to 30 per cent., steel with from traces to 1 per cent. and wrought iron with small fractions of 1 per cent.

In all these the silicon is combined as Si, not as SiO_2, though there may be a little SiO_2 included as intermixed slag, especially in wrought iron.

All of these metals are soluble in HNO_3, sp. gr. 1.2, except ferrosilicon, the silicon being oxidized to SiO_2, which passes wholly or in part into solution. Evaporation of the HNO_3 solution to dryness, baking and re-solution in HCl renders this SiO_2 only partially insoluble, a temperature of 250°C. not causing all the SiO_2 to separate.

To accomplish the complete separation of the silica by this means it is necessary to evaporate to dryness, bake as in the phosphorus determination, dissolve in HCl, and again *evaporate to complete dryness*, expelling all the HCl. On taking up again in HCl practically all of the silica is left insoluble. After dilution the solution may be filtered from the residue of silica + carbon, which after thorough washing, first with HC and then with water, may be ignited till the carbon is burned off, and weighed.

The silica thus obtained is rarely pure, and must be treated with H_2SO_4 and HF, or must be fused and the silica separated from the fusion. (See analysis of limestones.)

Hydrochloric acid or aqua regia may be used to dissolve the metal instead of HNO_3, but they do not attack ordinary iron so rapidly. Finally, solution in H_2SO_4 and HNO_3 and evaporation till fumes of H_2SO_4 are given off will cause a complete separation of the silica.

References:

For details of these various methods see—

Blair, "Chemical Analysis of Iron," Nitric Acid Method.

Troilius, "Notes on the Chemistry of Iron," p. 35. Sulfuric Acid Method.

Also *Trans.* Am. Inst. Mining Eng., X, 162, et seq., and 187, et seq.

When a nitric or hydrochloric acid solution containing silica is evaporated with H_2SO_4 the volatile acids will be expelled, and if the temperature is finally raised to near the boiling-point of the concentrated acid, the silica is completely dehydrated and becomes insoluble. Titanic acid, if present, passes into solution and the silica thus obtained is pure. The following method, slightly modified from one published by Dr. Drown, depends upon this fact. (Trans. Am. Inst. Mining Eng., VII, 346.)

Process for Pig-iron and Steel.—Weigh out 0.9386 gram of pig-iron or 4.693 grams of wrought iron or steel. Put into a casserole or dish and cover with a large watch-glass. Add carefully 30 c.c. of a cold mixture of 8 parts by volume of concentrated HNO_3, 5 parts of concentrated H_2SO_4 and 17 parts of H_2O (for the pig-iron) or 100 c.c. of a mixture of 35 parts of concentrated HNO_3, 15 parts of H_2SO_4 and 50 parts of H_2O (for the steel), or use the three-acid mixture given further on.

Warm till action ceases, then boil down rapidly on an iron plate or over the bare flame until the $Fe_2(SO_4)_3$ separates as a white mass; continue the heating until dense fumes of sulfuric acid are evolved. These have a peculiar suffocating odor, easily recognized. Their formation indicates the total expulsion of the HNO_3, and this is absolutely necessary in order to make the silica insoluble. In the case of steel low in silicon it is necessary to stir up the mass of ferric sulfate thoroughly or it may include silica not dehydrated and so cause loss. (Dudley). There will be danger of "spattering" unless the heating is carefully done, but if the dish is well covered this need cause no loss.

Now let cool, then add 10 c.c. of concentrated HCl and wash off the cover into the dish. Dilute to 150 or 200 c.c., cover, set over a burner and boil until all $Fe_2(SO_4)_3$ is dissolved. This can be recognized by the disappearance of the silky precipitate in the liquid. Continue the boiling for five minutes, as this will cause the solution to filter more easily. Then wash off the cover, and let the liquid stand until all the silica settles. Decant the clear liquid through a 7-cm. ashless filter, previously washed out with boiling water. Finally transfer and wash the residue with hot water. When partially washed, drop a little HCl on the filter and residue, then wash again with hot water till the filtrate no longer tastes acid. Without drying transfer the filter to a

crucible and ignite, gently at first, finally at high heat, until all the carbon (graphite) is burned and the silica is white. If this is done in a platinum crucible and over a blast lamp the burning off of the carbon need not take more than a few minutes.

It is important that the temperature be low at first, not exceeding a dull red until the paper and the amorphous carbon are burned out, as overheating at first will cause the carbon to lump together and it will then burn very slowly. During the final heating over the blast lamp keep the crucible partly covered. The burning may be hastened by directing a gentle current of oxygen gas into the crucible, but if due care is taken this is not necessary. If oxygen is used take care not to blow any particles of silica out of the crucible by forcing in the gas too rapidly.

The weight of the silica in milligrams divided by 2 in the first case or by 10 in the second gives the silicon in tenths of a per cent.

Notes on the Process.—If the above directions are followed exactly as to the dilution and boiling of the solution there will be no need of a filter pump to secure rapid filtration. Boiling with a large excess of water consolidates the silica so that it filters easily. The funnels and filter paper should be carefully selected; the former should have long and narrow stems that will fill with the liquid and produce a little suction. The funnel angle should be 60 degrees. A porous ashless paper like the Munktel "black label" is desirable. The precipitate of silica has no tendency to run through, so that a dense paper is not necessary.

The filter should be kept full while filtering the solution as, if it is allowed to empty, the paper will become clogged.

For pig-iron and ferro-silicons the following three-acid silicon mixture may be substituted for that already given, and will be found very efficient:

Water	150 c.c.
Sulfuric acid, sp. gr. 1.84	40 c.c.
Nitric acid, sp. gr. 14.2	80 c.c.
Hydrochloric acid, sp. gr. 1.19	60 c.c.

Mix in the order given and preserve for use. Twenty-five cubic centimeters of this mixture is enough for the "factor weight" of pig-iron (0.4693 gram). Evaporate to strong fumes of H_2SO_4, cool, add a little concentrated HCl, then add water and boil. With this mixture the silica filters particularly well. With steel where the silicon is in very

small amount it is necessary to test its purity. Add a drop of H_2SO_4 to the silica in the crucible and then a few drops of pure HF or a few crystals of NH_4F. Evaporate to dryness over a low flame, not allowing the liquid to boil, and ignite the residue strongly. The fumes of HF are poisonous, so the evaporation must be made under a good hood. The silica passes off as volatile SiF_4. If any residue remains, weigh it and deduct it from the total weight. The difference is SiO_2.

The following process is sometimes used for furnace control instead of the one just given.

The molten iron is chilled by pouring into water. This makes it very brittle. It is then pulverized in a steel mortar, dissolved in HCl, rapidly evaporated to dryness, taken up in HCl, diluted and filtered. Without drying, the filter is put into a platinum crucible, ignited in a steam of oxygen and weighed. The time required for this process is said to be 12 minutes.

In preparing the drillings for analysis, great care must be taken to keep them free from sand. This is difficult in the case of pig-iron, drillings from which should usually be cleaned.

This is easily accomplished by folding a sheet of paper over a magnet, then picking up the metal against the paper. The sand and other foreign particles are left behind. On drawing the magnet away from the paper the drillings will fall off and can be collected on a clean sheet of paper. All the drillings must be gone over and no considerable residue should remain. If much graphite-like substance is separated it may hold silicon belonging to the sample.

The drillings should be fine. Large fragments of metal dissolve slowly and may be left as hard grains in the silica, of course vitiating the result. If these lumps remain, add more acid and heat slowly until they dissolve.

Ferro-silicons may need to be pulverized till they go through bolting cloth before they will dissolve.

In weighing out, great care must be taken to secure an average of fine and coarse, as these usually differ in percentage of silicon.

To avoid unnecessary calculation it is usually convenient to weigh out the "factor weight" of the metal. SiO_2 contains 0.4693 Si; hence, if that weight in grams is taken for the analysis, each milligram of silica will indicate $\frac{1}{10}$ per cent. In low silicon irons or steel 0.9386 or some other multiple of the factor may be used.

Determination of Silicon in Ferro-silicon.—This material is not easily attacked by any of the above mixtures. If not too high in silicon, it can usually be dissolved by prolonged boiling

with aqua regia, adding fresh acid from time to time. Finally add 25 c.c. of dilute (1 :3) H_2SO_4, evaporate until fumes of sulfuric acid appear, and then finish as in the regular process.

Samples with over 10 per cent. silicon and which aqua regia will not dissolve are, according to Williams, best treated by fusing with six or eight times their weight of dry Na_2CO_3. Then proceed with the fusion, as in the determination of silica in a limestone. The metal must be very finely pulverized and not more than 0.5 gram taken. (Williams, Trans. Am. Inst. Mining Eng., XVII, 542.)

Instead of Na_2CO_3 alone, a mixture of Na_2CO_3 and $NaNO_3$ or Na_2O_2 may be used and the fusion conducted as described on page 60. But these reagents are much more injurious to the platinum than the carbonate, though more fusible and more rapid in their action.

Determination of Silica in Admixed Slag in Steel.—It is sometimes necessary to distinguish between the silicon combined in the steel as silicide and that combined as admixed slag. The following method depends upon the fact that iron is dissolved with iodine, while slag is unattacked. Silica formed from the silicide is soluble in caustic soda.

Process.—Place 5 grams of the drillings in a beaker, put the beaker in a dish filled with ice or snow and pour over the drillings 25 c.c. of ice-cold water. Add gradually about 30 grams of resublimed iodine stirring until the iodine is all dissolved. Keep the beaker covered with a glass and constantly surrounded with the scraped ice or snow. Stir the solution frequently, until the iron is all dissolved. Then add 100 c.c. of cold water; allow the insoluble matter to settle and decant the liquid through a small filter. Wash the insoluble residue several times with water by decantation. If any metallic iron remains, give the residue a further treatment with iodine. Transfer the insoluble matter to the filter, wash once with 1 : 20 HCl, then wash well with water a dozen times. Wash the residue on the paper back into a platinum dish, add enough NaOH to make a 10 per cent. solution, and heat to boiling for several minutes. This dissolves any precipitated silica formed from the silicide of the steel. Decant the liquid through a small filter, and again boil the insoluble matter with 50 c.c. of 10 per cent. NaOH solution. Filter this

through the same paper, wash several times with hot water, and, finally, wash with dilute HCl (1 : 20), and again several times with hot water. Ignite and weigh as Slag and Oxide. In *this then* determine the silica as in a steel.

CHAPTER VI

THE DETERMINATION OF MANGANESE

There are two classes of material to be considered: first, ores, slags and metals high in manganese, such as manganite and ferro-manganese containing from 15 to 90 per cent. Second, ordinary iron ores, pig-irons and steel, containing from a trace up to about 3 per cent. of manganese. These call for a somewhat different treatment.

The Acetate Process

This is a standard process. It depends upon the separation of the iron from the manganese as a basic acetate. The precipitate will contain also any alumina, titanic acid and phosphoric acid present in the solution. To get a good separation it is essential that the process be conducted very precisely in respect to certain details.

The reactions are as follows: When Na_2CO_3 is added to the solution containing $FeCl_3$, $MnCl_2$ and excess of HCl, the free HCl is first neutralized, then the Na_2CO_3 begins to act on the $FeCl_3$, forming what is practically a solution of ferric hydroxide in ferric chloride. It has been shown that 1 part of ferric chloride will hold in solution in this way as much as 10 parts of ferric hydroxide, perhaps as $Fe_xCl_y(OH)_z$.

This solution is very dark red in color and probably contains a complex compound in which the chlorine of the ferric chloride is partly replaced by hydroxyl. Upon the addition of sodium or ammonium acetate the chlorine remaining in this compound is replaced by the acetic acid radical and sodium or ammonium chloride is formed in the solution. When the solution is heated, this complex substance is decomposed; the iron being completely precipitated as hydroxide retaining only a little acetic acid. This is the so-called basic acetate precipitate. The solution now contains free acetic acid. If exactly the right amount of sodium acetate has been added, the manganese will be left in the solution and none of it will be found in the precipitate. If too much acetate has been added some manganese dioxide may precipitate with the iron. The excess of sodium acetate has the effect of decreasing the acidity of the solution by introducing a large amount of the acetate-ion, thus decreasing the ionization of the already only slightly ionized acetic acid

set free by the hydrolysis of the basic acetate of iron. This decrease in acidity may make it possible for the MnO_2 to precipitate.

From these facts it is evident that as much sodium carbonate should be added as possible without causing a permanent precipitate, and only as much sodium acetate added as is necessary to replace the chlorine remaining in combination with the iron and make the proper acidity.

The dissociation by boiling depends upon hydrolysis and is only complete in very dilute solution; at least 500 c.c. of water must be present for each gram of iron. The reaction may be written:

$$Fe_x(OH)_y(CH_3COO)_z + ZHOH = XFe(OH)_3 + ZCH_3COOH.$$

The Acetate Process for the Determination of Manganese in Ores with High Percentages

The process depends upon the separation of the iron and alumina as basic acetates, precipitation of the manganese as MnO_2 by bromine, resolution of the precipitate and determination of the manganese as pyrophosphate.

If bromine water is added to the filtrate from the basic acetate, the manganese is completely precipitated as MnO_2, provided an excess of sodium acetate over that required to convert $MnCl_2$ into acetate is present. Nickel and cobalt, if present, will also precipitate. If chromium is present some will stay with the iron and some will go with the manganese.

If ammonium salts are present, the MnO_2 will only separate when the solution is made alkaline and then not completely. The iron solution must contain no *ferrous salt* or a red "brick dust" like, slimy precipitate will form, and the filtrate will be cloudy and deposit iron.

The process is perfectly satisfactory provided all details are carefully followed.

Process for Ores.—Dissolve $\frac{1}{2}$ gram of the ore in 15 c.c. concentrated HCl, dilute and filter as in the iron assay.

Evaporation to dryness is usually unnecessary, few ores containing soluble silicates. When such occur, as in slags, dissolve in dilute acid, evaporate to dryness, add HCl and then water.

If no chlorine is given off when the ore is dissolved, owing to the absence of MnO_2, ferrous iron may be present. In this case add a crystal of $KClO_3$ and boil until all the chlorine is expelled.

When the ferric chloride solution is evaporated to dryness in the presence of organic matter, a slight reduction to ferrous salt often occurs, hence, in this case the solution should be oxidized

after filtration by adding a little $KClO_3$ or HNO_3. The solution must be boiled till all the chlorine is expelled or manganese will precipitate with the iron in the subsequent separation.

To the filtrate, add a solution of sodium carbonate carefully until a slight permanent precipitate forms. Redissolve this with a few drops of HCl, giving each drop two or three minutes to act, and stopping as soon as the solution clears.

Now dilute to about 300 c.c., add 1 gram sodium acetate, cover the beaker and boil vigorously till the iron separates. Should it not come down promptly add a solution of Na_2CO_3 drop by drop until the precipitation is complete. The liquid must be distinctly acid when tested by a slip of litmus paper. Let the precipitate settle clear and decant the liquid through a 9 cm. filter, pouring off as closely as possible, add 150 c.c. of boiling water, let settle, decant as before, and finally transfer the precipitate and wash once with hot water. Wash it off the filter back into the beaker. Dissolve it in the least possible quantity of HCl and repeat the precipitation exactly as before. Transfer the precipitate to the filter and wash well with *hot water*. Test this precipitate for manganese by fusing a little of it with Na_2CO_3 and $NaNO_3$ on a platinum wire. If not free from manganese a third precipitation will be necessary; or the manganese in the precipitate may be determined by the bismuthate-arsenite method.

The filtrate will amount to about a liter. It should be perfectly clear and colorless. Concentrate it to about 500 c.c., then add 10 grams of sodium acetate and an excess of bromine water. Warm until the MnO_2 has settled and the liquid is clear. Filter on a 7 cm. filter and wash well with hot water.

Wash the precipitate off the filter into a beaker. Now wash the filter paper with dilute HCl, in which a small crystal of oxalic acid is dissolved, receiving the filtrate in the beaker containing the MnO_2. This will dissolve any MnO_2 adhering to the paper.

Heat the beaker containing the MnO_2 and HCl and add oxalic acid solution drop by drop until the MnO_2 is dissolved.

Now dilute to about 150 c.c. and add NH_4OH until the solution is just distinctly alkaline, putting a small strip of litmus paper in the solution as an indicator. If iron is present a slight precipitate will form. Now drop in acetic acid until the solution is just acid. Boil the solution. If any precipitate of

$Fe(OH)_3$ separates, filter it off and wash precipitate and filter with hot water.

Unless this precipitate is light red in color and very small in amount, dissolve it in a few drops of HCl, add H_2O, then NH_4OH, then acetic acid as before. Boil till the precipitate separates and filter into the original solution. This re-solution is essential in most cases, and need delay the work but a few moments. The object of the oxalic acid is to reduce the MnO_2 to MnO, and so make it dissolve quickly. MnO_2 is very slowly attacked by dilute HCl alone.

To the filtrate, now perfectly clear and colorless, add an excess of a solution of microcosmic salt ($NaHNH_4PO_4.4H_2O$). Now heat to boiling, add NH_4OH drop by drop as fast as the precipitate formed by each addition becomes "silky" in appearance, stirring all the time to prevent bumping. When no more precipitate forms add enough NH_4OH to make the solution smell slightly of NH_3, and boil till the precipitate is completely silky and settles quickly. Now cool the liquid and filter. Wash the precipitate with water containing a few drops of NH_4OH. Ignite and weigh as $Mn_2P_2O_7$, containing 0.3868 Mn.

The acetate of soda used must be tested for manganese. If any is found, dissolve the salt in water, add bromine water and boil till all the bromine is expelled. Filter the solution from the MnO_2 thus separated and use it instead of the solid salt.

Process for Spiegel Eisen and Ferro-manganese.—Take 0.500 gram of the powdered metal, dissolve in 10 c.c. HNO_3, sp. gr. 1.2, plus 5 c.c. HCl, evaporate to dryness and "bake," then dissolve in 10 c.c. of concentrated HCl, add a little bromine water (to reoxidize any FeO formed), boil down till all excess of bromine is gone and most of the HCl evaporated. Dilute, filter if necessary and precipitate the iron and determine the manganese as by the method for ores.

Some ores and spiegel irons contain copper and nickel. These will come down with the MnO_2 in part at least. They should be separated by H_2S, which will precipitate nickel, cobalt, copper and zinc, but not manganese from a solution containing a slight excess of acetic acid. This may be done in the original acetate filtrate. The solution must be boiled till all H_2S is expelled before adding bromine.

The Acetate Process for Ores Low in Manganese

In this case it is desirable to work upon larger amounts of material. The filtration and washing of a large basic acetate precipitate is very troublesome, and can be avoided by taking an aliquot part of the solution after the precipitate has settled. The error introduced by neglecting the volume of the precipitate is inappreciable when the percentage of manganese is small.

A single precipitation of the iron is entirely sufficient, provided care be taken to avoid excess of sodium acetate.

Extreme care in measuring the solution, as well as in keeping the temperature constant, is also superfluous when less than 3 per cent. of manganese is present and the volumes are kept large; 10 c.c. on a liter causing an error of only 0.03 per cent.

The precipitate by bromide is MnO_2. On ignition at moderate temperatures with ample access of air, it changes principally to Mn_3O_4, though the exact nature of the oxide produced varies with the conditions of heating. This precipitate also usually retains small amounts of sodium salts. For these reasons the percentage of manganese which it contains is always a little uncertain. As the variations are limited to a small percentage of the weight of the precipitate, the results obtained by weighing it directly will be sufficiently accurate for all ordinary work, where but little manganese is present.

Process of Analysis.—Dissolve 4 grams of the ore in 30 c.c. concentrated HCl exactly as in the iron assay. If there is any ferrous iron present, add about 1 c.c. of HNO_3 to completely convert it to ferric chloride. Boil the solution until the excess of HNO_3 is decomposed and the chlorine expelled. The evaporation need not go so far that insoluble iron salts separate; should such form, add more HCl and heat until they dissolve. Add water, warm and filter from the residue.

Take a large Erlenmeyer flask, one which will hold when quite full 2400 c.c. Dry it, then measure into it exactly 2000 c.c. of water; this should reach up into the narrower portion of the flask. Paste a thin strip of paper on the glass to exactly indicate the level of the liquid. The flask must be set on a level desk, and the place it stands on as well as the position of the paper mark noted, so that it can be subsequently returned *to the same position*

Now transfer the solution of the ore to the flask, and dilute it to about 1700 c.c. Then add a solution of Na_2CO_3 gradually until the liquid begins to grow dark red. Continue to add the reagent drop by drop, shaking the flask after each addition until the liquid is very dark in color and the precipitate formed redissolves very slowly. The object is to reach a point just short of that at which the iron is precipitated. The operation requires practice. Should the point be overstepped, add a little HCl, and when the liquid becomes clear, neutralize again; but in this case, in the writer's opinion, the iron precipitate is more likely to contain manganese.

Now add 6 grams of pure sodium acetate. Set the flask on a hot plate and boil the solution vigorously.

The iron should immediately separate as a bulky, red precipitate. If it fails to do so at once, drop in very cautiously a dilute solution of Na_2CO_3 until the separation is complete. Now boil a few minutes longer, then remove the flask to the place where it stood when it was graduated, placing it in the same position, and fill it exactly to the mark with cold water. Stir the liquid thoroughly with a long rod, then let it settle. As soon as it is clear pour off 1 liter into a graduated flask. This whole operation can be done so quickly that the liquid will not cool materially.

Filter the measured portion of the liquid. The filtrate should be colorless and distinctly acid to litmus paper.

Concentrate the filtrate to about 500 c.c. Add 5 grams of sodium acetate and boil. Should any precipitate form filter it off, dissolve it in HCl containing a little oxalic acid, add a solution of Na_2CO_3 until a slight permanent precipitate forms, then acetic acid till just acid. Boil this liquid, filter from any precipitate, and add the filtrate to the main solution.

Finally add bromine water, warm until the MnO_2 settles completely, filter, wash well with hot water, ignite and weigh as Mn_3O_4 containing 0.7203 Mn. Calculate the result on 2 grams of ore taken.

Should the ore leave but little residue this need not be filtered off, but may go into the flask with the solution. In applying this process to slags and ores containing decomposable silicates, the HCl solution must be evaporated to dryness, taken up again in HCl, HNO_3 added and boiled off as usual.

If care be taken in the neutralizing no precipitate will form on concentrating the filtrate from the iron and delay will be avoided.

Should the ore contain nickel or cobalt, these will contaminate the manganese precipitate and the results will be inaccurate. In this case the precipitate of MnO_2 must be redissolved in HCl containing a little sodium sulfite. The solution is boiled till free from SO_2, then cooled and nearly neutralized by Na_2CO_3, a little sodium acetate added and the nickel and cobalt precipitated by H_2S. In the filtrate from these sulfides the manganese can be determined either by precipitation with bromine or as phosphate.

The Acetate Process Applied to Pig-iron and Steel.—Dissolve 4 grams in 50 c.c. HNO_3, sp. gr. 1.2, add 10 c.c. concentrated HCl. Evaporate to dryness and bake. Redissolve in 25 c.c. concentrated HCl, add a little HNO_3, boil and proceed as with ores low in manganese. Filtration from the insoluble residue is unnecessary.

References on the Acetate Process:

Blair, "The Chemical Analysis of Iron."

Trans. Am. Inst. Mining Eng., X, p. 101.

Sillimans, *Am. J. Sci.*, (11) XLIV, p. 216, on the determination as phosphate.

Ber., 1900, p. 1019.

The Ford-Williams Method for Manganese Separation of Manganese by Chlorates

When potassium or sodium chlorate is added to a solution of manganese in hot concentrated HNO_3 the manganese is all precipitated as MnO_2. To secure complete and rapid precipitation the chlorate should be added to the boiling solution in successive small portions, the HNO_3 must be in large excess and concentrated, HCl must be absent, and there must be at least as much iron as manganese in the solution. The precipitate may be filtered off on an asbestos filter and washed with concentrated HNO_3. MnO_2 is entirely insoluble in cold concentrated HNO_3 provided this contains no lower oxides of nitrogen ("red fumes"); if these are present, that is, if the HNO_3 is not *perfectly colorless*, the MnO_2 will be reduced and dissolved.

After washing, the precipitate may be redissolved and the manganese determined gravimetrically as pyrophosphate or volumetrically by measuring the oxidizing power of the MnO_2 on ferrous sulphate or oxalic acid.

The precipitate contains a little iron but is free from other impurities.

When the solution to which the chlorate is added contains any HCl, this is first acted upon and broken up before the MnO_2 will separate, chlorine being driven off and water formed by the oxidation. This will result in weakening the HNO_3, and hence in this case more HNO_3 must be present to prevent too great loss of strength.

The method is especially adapted to the determination of manganese in steels and irons low in silicon and dissolving in HNO_3 without residue.

If SiO_2 is present in the solution it may separate in a gelatinous form which prevents filtration and coats the particles of the precipitate so that they dissolve with difficulty. It should be removed by the addition of a few drops of hydrofluoric acid to the liquid after the precipitation of the MnO_2. Sodium chlorate is preferable to potassium chlorate because its greater solubility makes it easier to wash out of the precipitate.

Process for Steel Low in Silicon.—Dissolve 5 grams in 60 c.c. HNO_3, 1.2 sp. gr., in a 200 c.c. beaker. Evaporate to 25 c.c., then add 100 c.c. of *colorless concentrated* HNO_3. Set on an iron plate and heat to incipient boiling. Now drop in powdered $NaClO_3$ or $KClO_3$, a little at a time, adding each portion when the effervescence produced by the preceding portion has ceased. By the time 2 to 2½ grams have been added the MnO_2 will have separated as a fine brown powder. Now add ½ gram more of the chlorate and boil gently for 10 minutes. If any SiO_2 is present in the solution, after three or four minutes boiling add a few drops of pure HF. Then add 1 gram more of the chlorate and 25 c.c. concentrated HNO_3 and boil 10 minutes longer. Remove from the plate and cool by setting the beaker in water. When the MnO_2 has settled, filter without dilution, through an asbestos filter in a Gooch crucible. Finally transfer the MnO_2 to the filter and wash beaker and filter with *colorless concentrated* HNO_3 three or four times, or until the filtrate is colorless. This can be done without using more than 15 or 20 c.c., adding only a little each time and letting each portion run through before adding the next. Finally wash with a little cold water. If the HNO_3 is colored by lower oxides of nitrogen (from standing and the action of light), it can be purified by blowing a strong current of air through it until it becomes colorless.

After washing the MnO_2 with cold water till the acid taste is gone from the filtrate (letting each successive portion of water

run entirely through before adding the next, so as to not use in all more than 20 c.c.) wash the asbestos and precipitate back into the beaker (which always has some MnO_2 adhering to it).

Volumetric Determination of the Mn.—This process consists in dissolving the MnO_2 in a measured excess of an acid solution of ferrous sulfate of a known strength. Each molecule of MnO_2 changes two molecules of ferrous sulfate to ferric sulfate. The amount of ferrous sulfate remaining is then determined by a standard solution of potassium permanganate. The reactions are as follows:

1. $MnO_2+2FeSO_4+2H_2SO_4=MnSO_4+Fe_2(SO_4)_3+2H_2O$.
2. $10FeSO_4+2KMnO_4+8H_2SO_4=5Fe_2(SO_4)_3+K_2SO_4+2MnSO_4+8H_2O$.

The process requires first, a solution of potassium permanganate of a known strength; second, a solution of ferrous sulfate in dilute sulfuric acid. The strength of this is determined by titration with the permanganate solution.

Preparation of the Permanganate Solution.—Dissolve 1.151 gram of pure $KMnO_4$ in water and dilute to 1 liter. One cubic centimeter of this solution will have the same oxidizing power as 0.001 gram of manganese in the form of the brown precipitate (MnO_2). Check the solution against pure iron or pure ammonium ferrous sulfate $(NH_4)_2Fe(SO_4)_26H_2O$. Dissolve 0.1425 gram of the salt in 50 c.c. of water containing 2 c.c. of H_2SO_4. This should consume just 10 c.c. of the permanganate solution. Run in the solution until the last drop gives a permanent pink color.

If more or less than 10 c.c. is required, calculate the amount of Mn to which each cubic centimeter of the permanganate is equivalent by the proportion, $0.001:x=n:10$, n being the number of cubic centimeters of solution used in the test, and x the required value.

Preparation of the Ferrous Sulfate Solution.—Dissolve 20.18 grams of pure crystallized ferrous sulfate ($FeSO_47H_2O$) in about 500 c.c. of water, to which 25 c.c. of concentrated H_2SO_4 has been added, and then dilute to 1 liter.

Determine its strength against the permanganate solution by measuring 15 c.c. with a pipette into a beaker, adding about 25 c.c. of water and 1 c.c. of H_2SO_4 and then running in the permanganate till the pink color is permanent. About 30 c.c. should be required. This value must be determined frequently

as the solution of ferrous sulfate alters rapidly from the oxidizing action of the air. In large amounts it is best kept in a carboy and covered with a layer of kerosene oil to keep out air. The solution can be preserved in this way for some time with but little alteration, and can be drawn out by a siphon as needed.

From the two formulas already given we have the relations between the MnO_2, $FeSO_4$ and $KMnO_4$ as follows:

One atom of Mn in the form of brown precipitate (MnO_2) will oxidize two atoms of Fe as ferrous sulfate. Two molecules of permanganate will oxidize ten atoms of Fe as ferrous sulfate, that is to say, two molecules of permanganate will oxidize the same amount of iron as will five molecules of MnO_2 containing five atoms of manganese. Therefore, to find how much $KMnO_4$ will be needed to have the same oxidizing power as 0.001 gram of Mn in the form of the brown precipitate we have the proportion:

5 atoms Mn : 2 mol. $KMnO_4 = 275 : 316.3 = 0.001 : x$, which gives $X = 0.00115$ gram, the amount of $KMnO_4$ to be dissolved in 1 c.c. if 1 c.c. is to be equivalent to 0.001 gram Mn as "brown precipitate." This is 1.151 gram in a liter.

To determine the amount of iron, or of ammonium ferrous sulfate to which 1 c.c. is equivalent, we have:

1 atom Mn : 2 atoms $Fe = 55 : 112 = 0.001 : x$, in which x is the required amount of iron. The value of x is 0.002034. To determine the amount of the ammonium ferrous sulfate, as this contains one-seventh of its weight of iron, multiply the value of x by $7 = 0.01425$ for 1 c.c., or the figure given in the directions for 10 c.c.

That 15 c.c. of the ferrous sulfate solution may be equivalent to 30 c.c. of the permanganate it must contain 0.06102 Fe. This corresponds to 20.18 grams of $FeSO_4$, $7H_2O$ to the liter.

Determination of the MnO_2.—To the asbestos and MnO_2 in the beaker, add the solution of ferrous sulfate from a burette 5 c.c. at a time until, after stirring and warming, the MnO_2 is *completely* dissolved. It is best to take the same burette used in standardizing. Break up all lumps of asbestos and precipitate with a glass rod as they may inclose undissolved particles of MnO_2. Now add a little water and run in the permanganate solution till a pink color is produced, not disappearing under two

or three minutes. Read the burette and deduct the amount used from that to which the amount of ferrous sulfate taken would have been equivalent; the difference is equivalent to the Mn present in the precipitate. This, corrected by the factor for the permanganate solution, will give the amount of Mn in milligrams.

As an example: Suppose that 5 c.c. of ferrous sulfate solution equaled 9.6 c.c. of permanganate solution, and 10.3 c.c. permanganate equaled 0.1425 gram of ammonium ferrous sulfate. If 15 c.c. of ferrous sulfate solution were added to dissolve the MnO_2 and the permanganate required to oxidize the excess was 4.5 c.c., then the calculation is as follows:

$3 \times 9.6 = 28.8$ = the permanganate equivalent to the $FeSO_4$ used.
4.5 = the "titer back."

24.3 = the number of cubic centimeters of permanganate equivalent to the precipitate.

$24.3 : x = 10.3 : 10$ (x being the true amount of correct permanganate).
$x = 23.6 = 0.0236$ gram Mn in the precipitate.

Process for Ores.—Take 5 grams. Dissolve in 50 c.c. of concentrated HCl, evaporate to dryness, avoiding a temperature above 100°; add 20 c.c. HCl, and then water. When dissolved, filter into a No. 2 beaker. Add 50 c.c. concentrated HNO_3, evaporate to a syrup, then add 100 c.c. of concentrated HNO_3 and proceed as before.

Process for Pig-iron.—Dissolve 5 grams of the metal in HNO_3, sp. gr. 1.2, taking about 60 c.c. Then add 25 c.c. HCl, evaporate to dryness and bake. Dissolve in HCl, filter from the SiO_2, and to the filtrate add 0.2 gram ammonium fluoride or a few drops of hydrochloric acid. Then add 50 c.c. of HNO_3. Concentrate to a syrup, add 100 c.c. HNO_3 and proceed as before. The hydrofluoric acid expels traces of SiO_2 from the solution and greatly accelerates the filtration from the MnO_2 (E. F. Wood).

The above process, carefully conducted, is capable of giving very accurate results, but it requires practice and should be tried on metals in which the manganese has been carefully determined by another method until the two give concordant results.

Process for Ferro Manganese and Ores High in Manganese.—The permanganate solution should be standardized by working on a metal of known percentage of manganese, as the composition of the precipitate is considered by some chemists not to be exactly MnO_2, but by thus standardizing in the same way that the ore is analyzed, all risk from this source is avoided. Where only small amounts of manganese are present this source of error is unimportant.

The Volhard process, however, is better adapted to high manganese materials and is more rapid.

One slight objection to the chlorate process is the large amounts of expensive acids required. To avoid this the process can be worked on smaller amounts of substance, but great care and skill are then needed to secure close results. All measurements and titrations must be very exact.

Process.—Take 1 gram of iron or steel, dissolve it in 15 c.c. of HNO_3, sp. gr. 1.2. Evaporate to 10 c.c., add 35 c.c. HNO_3, sp. gr. 1.42, and after precipitation and boiling, 10 c.c. more, reduce the $KClO_3$ to about 1 gram, filter, wash and proceed with the volumetric determination of the precipitate.

It is possible to determine the MnO_2 in the presence of the nitric acid without filtering it off by proceeding as follows: After precipitating the MnO_2, cool the acid and dilute it to about 400 c.c. with cold water. Now add the ferrous sulfate solution to dissolve the MnO_2 directly, and immediately titrate with the permanganate. In working in this way the excess of potassium chlorate must be completely destroyed before diluting the solution and the temperature of the liquid kept quite low when adding the ferrous sulfate. Great care in these points is necessary in order not to start the reaction between the HNO_3 and the $FeSO_4$ which would vitiate the results. The permanganate solution should be standardized under similar conditions.

References:

Trans. Am. Inst. Mining Eng., IX, p. 397.
Trans. Am. Inst. Mining Eng., X, p. 100.
Trans. Am. Inst. Mining Eng., XII, p. 73.
Trans. Am. Inst. Mining Eng., XIV, p. 372.
J. Am. Chem. Soc., 1898, p. 504.
Am. J. Sci., V, (4) 260.
J. Anal App. Chem., II, p. 249.

Volhard's Process for Manganese

This is a volumetric process depending upon the reactions between potassium permanganate and manganous salts by which all the manganese is precipitated as MnO_2.

$$3MnSO_4+2KMnO_4+2H_2O=5MnO_2+2KHSO_4+H_2SO_4.$$

The method is especially applicable to high manganese ores. For low manganese ores and for iron and steels the bismuthate-arsenite method is best.

The solution must be neutral or very nearly so. The titration must be made with the solution nearly at the boiling-point and very dilute or the precipitate will not settle quickly and it will be difficult to see the end reaction. For the same reason the solution must be vigorously shaken or stirred and the permanganate added rather slowly, especially at first. Too rapid addition of the permanganate will cause the MnO_2 to precipitate on the glass, forming a firmly adherent yellow-brown stain which makes it very difficult to see the final pink color produced by the excess of permanganate when the titration is finished.

The permanganate solution used in the iron assay will serve for manganese. If 1 c.c. equals 0.01 Fe, then 1 c.c. will equal 0.002951 Mn.

In this process the iron is separated from the manganese by means of zinc oxide. ZnO precipitates the iron completely as hydroxide from a dilute solution of ferric sulfate, while manganese sulfate is not affected and remains in the solution.

Sufficient ZnO must be added to neutralize any free sulfuric acid present as well as to precipitate the iron.

The separation of the iron is really due to hydrolysis, the ZnO serving to keep the solution neutral. The reaction is:

$$Fe_2(SO_4)_3+3ZnO+6HOH=2Fe(OH)_3+3ZnSO_4+3H_2.O$$

The ZnO must not contain any alkali, as Na_2CO_3, as this would precipitate manganese.

Process for Ores.—Take 0.5 gram of the sample; ignite it to redness if carbonaceous matter is present; then transfer it to a casserole and digest with 15 c.c. of concentrated HCl. If any ferrous iron is present add a few small crystals of $KClO_3$ to oxidize it to the ferric state. Finally boil until all free chlorine is expelled. Now add 10 c.c. of dilute H_2SO_4 (1:1) and evaporate till fumes of H_2SO_4 begin to come off, then cool the casserole and add 75 c.c. of water. Warm till all of the ferric sulfate goes into solution and then transfer to a 200 c.c. graduated flask.

Add a solution of Na_2CO_3 to the contents of the flask until most of the free acid is neutralized, cool the contents of the flask if at all warm and then add ZnO suspended in water, small portions at a time and shaking after each addition, till the iron separates as hydroxide. Dilute to 200 c.c. and mix thoroughly. Let the precipitate settle and then filter through a dry filter. Collect 100 c.c. of the filtrate rejecting the first few cubic centimeters that run through. Transfer this portion to a large flask, dilute it to 300 c.c., add exactly two drops of HNO_3, sp. gr. 1.2, and heat to boiling. Titrate with $KMnO_4$ shaking well after each addition, till a faint pink remains, which does not disappear for a few minutes. From the strength of the $KMnO_4$ and the number of cubic centimeters required, calculate the percentage of Mn.

The titration must be made rapidly so that it will be finished before the solution cools. If by accident the solution cools so that the MnO_2 separates badly before finishing the titration, heat it again quickly but not to boiling.

Run a blank on the reagents to test them for manganese or any other substance which would reduce the $KMnO_4$ solution.

Process for Pig-iron and Steel.—Weigh out 1 gram of the well-mixed borings into a casserole. Add gradually 25 c.c. of HNO_3, sp. gr. 1.2. When the metal is dissolved evaporate to dryness and bake for a few minutes, then take up in 10 or 15 c.c. of HCl and heat till the iron salts go into solution. Now add 10 c.c. of dilute H_2SO_4 (1:1) and evaporate till dense fumes of H_2SO_4 are given off, keeping the dish well covered to avoid loss from spattering, and to avoid the formation of dry salts on the sides of the casserole. Cool, add 100 c.c. of water, and warm till all the ferric sulfate goes into solution. Transfer to a 500 c.c. flask, nearly neutralize with Na_2CO_3, cool, and then add the zinc oxide, suspended in water as described before, till the iron is precipitated. Dilute to 500 c.c. mixing the contents of the flask thoroughly. Filter off 250 c.c. Add to this two drops of HNO_3, sp. gr. 1.2, heat to boiling and titrate carefully with $KMnO_4$ till a faint pink color is permanent.

Notes on the Process.—Where the amount of manganese in the sample is less than 0.7 or 0.8 per cent. the process is not satisfactory, unless more of the sample is taken, since the precipitate will not clot and settle

properly if there is less than 5 or 6 mg. of manganese in the liquid. Therefore, in applying the process to ores or metals quite low in manganese, enough sample must be weighed out so that there shall be at least this amount of manganese in the liquid titrated.

As more than a trace of free acid interferes with the titration, the amount of HNO_3 added must not exceed that indicated or the precipitate will settle badly and the end point be indistinct. Evaporation with H_2SO_4 is necessary to destroy the carbonaceous matter as well as to expel the HNO_3, both of which may affect the titration.

Instead of taking 1 gram for the analysis, it is usually more convenient to take such an amount of the sample as will make 1 c.c. of the permanganate equivalent to 1 per cent. of manganese. This amount can be calculated from the iron standard of the permanganate. Thus, if 1 c.c. of the $KMnO_4$ equals 0.01 Fe, take 0.5902 gram of the sample for the process, then the half of the solution taken for the titration will contain 0.2951 gram of the sample and each cubic centimeter of permanganate used will obviously represent 1 per cent. of Mn.

For steels low in carbon the Volhard method has been modified by omitting the evaporation with H_2SO_4 and not filtering from the precipitate of ferric hydroxide produced by the ZnO, but instead simply decanting an aliquot part of the somewhat turbid liquid and titrating directly in the presence of the nitrates. In this case the permanganate should be standardized on a steel of similar kind in which the manganese has been determined gravimetrically. High carbon steel should be evaporated to dryness with HNO_3 and baked.

References:

Stone, *J. Am. Chem. Soc.*, 1896, p. 228.
Auchy, *J. Am. Chem. Soc.*, 1896, p. 498.
J. Ind. Eng. Chem., I, p. 607.
Orthey, *Z. anal. Chem.*, XLVII, 547–560.

Volhard's method as above given has the defect that results are apt to run low. The reason is supposed to be that the MnO_2 carries down with it some MnO. Fischer's modification of Volhard's method is designed to overcome this difficulty. It is as follows:

Weigh out 1 gram of the ore, transfer it to a beaker and dissolve in 25 c.c. of HCl, sp. gr. 1.12. Boil till all iron is dissolved and without cooling add a 1-gram tabloid of $KClO_3$. Drive off the free chlorine by several minutes' boiling and, while still boiling, add cautiously a little Na_2CO_3. The violent evolution of carbon dioxide completes the removal of chlorine. Transfer to a large flask and dilute to 500 c.c., add NaOH solution till a

slight precipitate appears which is dissolved in a few drops of dilute H_2SO_4. Now add 10 grams of $ZnSO_4$, heat to boiling and add 1 gram of ignited ZnO. Titrate with $KMnO_4$ with vigorous shaking and with the liquid kept at boiling. When a permanganate color appears, cool somewhat and add 1–2 c.c. of glacial acetic acid when the color will disappear. Now finish the titration in the hot but not boiling solution. The permanganate color should persist after the solution has been shaken several times. The color will then persist for one to two hours.

References:
Fischer, *Z. anal. Chem.*, XLVIII, 751–760.
Cahen and Little, *Analyst*, XXXVI, 52–59.

The Bismuthate-arsenite Method for Manganese

This method for manganese, when it is present in moderate amounts (up to 2.5 per cent.) is, in the writer's opinion, the most accurate known. No elements interfere if the process is properly carried out. The delicacy of the reaction between manganese and bismuthate in HNO_3 is remarkable; as little as 0.00001 gram in 50 c.c. can be easily detected. HCl must be absent as it is ruinous to the accuracy of the results.

The method is based on the fact that in a cold HNO_3 solution of the proper strength manganese is oxidized to permanganic acid by the bismuthate. This is very stable in cold HNO_3, sp. gr. 1.135, but in hot solution the excess of bismuthate is decomposed and dissolved and then the permanganate is destroyed. In the cold, however, the excess of bismuthate may be filtered off and the permanganate titrated by a standard reducing agent.

The reactions may be written:

$$5Bi_2O_4+2Mn(NO_3)_2+26HNO_3=10Bi(NO_3)_3+2HMnO_4+12H_2O.$$
$$2HMnO_4+5Na_3AsO_3+4HNO_3=5Na_3AsO_4+2Mn(NO_3)_2+3H_2O.$$

Process for Iron and Steel.—If the sample does not contain over 1 per cent. Mn, use a 1 gram sample; if 1 to 2 per cent., use a 0.5 gram sample. Dissolve in 45 c.c. water and 15 c.c. HNO_3, sp. gr. 1.42, in a 150 c.c. flask. When dissolved boil until nitrous fumes are gone. Set the flask off the hot plate and cool a moment, then add 0.25 gram of "bismuthate" and shake and continue adding the bismuthate in 0.25 gram lots until a permanganate color comes which persists after a few minutes' boiling. This indicates complete oxidation of the solution. On boiling,

the permanganic acid is gradually decomposed to MnO_2. Now add a few small crystals of KNO_2 to dissolve the MnO_2 and boil the solution several minutes to expel nitrous fumes. A little Na_2CO_3 added now will aid the expulsion of the fumes. Add water to bring the volume up to its original volume and cool to tap-water temperature. When cold add 0.5 gram of "bismuthate" and shake the flask well. Add 20 c.c. of water and again shake, then filter through asbestos, preferably after settling, and wash several times with distilled water.

Titrate the filtrate with standard arsenite solution. If the manganese is high, a little MnO_2 may appear at the end but this does no harm as the titration is continued until the brown MnO_2 disappears. This only takes a drop or two after the pink disappears.

Arsenite Solution.—Add to 0.908 gram pure As_2O_3 in a beaker, hot Na_2CO_3 solution until the As_2O_3 all dissolves, then dilute to a liter. One cubic centimeter should be equal to 0.0002 gram Mn. To standardize, treat a sample of steel with known Mn content as above described. Or dissolve 0.5754 gram $KMnO_4$ in a liter of water, pipette off 25 c.c. and treat as a sample. $KMnO_4$ has 34.76 per cent. Mn so 25 c.c. of the solution contains 0.005 gram Mn and should require 25 c.c. of the arsenite to titrate it.

Notes on the Process.—It is necessary to add the bismuthate to the hot HNO_3 solution until all carbon, sulfur, etc., are oxidized as well as the manganese. Otherwise results will run low. This complete oxidation is indicated when the MnO_2 formed when the $HMnO_4$ is decomposed by boiling, remains after boiling a minute or so.

Chromium is partly, and vanadium completely, oxidized to the higher forms H_2CrO_4 and H_3VO_4 by the bismuthate in cold solution. These do not harm if the titration is carried out as above directed. If, however, titration is carried out by adding an excess of arsenite or other reducing agent and then oxidizing back to standard $KMnO_4$, the results will be high if chromium or vanadium are present as the chromic acid and vanadic acid will be reduced by the arsenite. The titration should be carried out by adding the arsenite until the permanganate color just disappears.

The best material for filtering off the Bi_2O_4 is asbestos and glass wool made as follows: Shake together in a flask with water sufficient glass wool to fill a funnel one-fourth full and about the same amount of pure

asbestos fiber. Pour into a funnel and wash out all HCl. This filtering medium does not easily stop up and yet filters perfectly. It may be used for a large number of filtrations without changing.

When pig-irons are being analyzed they should be filtered when dissolved in order to remove the graphite. In the analysis of white irons it will be necessary to treat the solution several times with bismuthate in order to oxidize the large amount of combined carbon present. The solution should be nearly colorless when cold.

Process for Iron Ores.—Treat 1 gram in a beaker with 20 c.c. HCl until all iron is in solution. Add 4 c.c. H_2SO_4 and evaporate until the H_2SO_4 fumes freely, taking particular care that all the HCl is removed. Cool and dissolve in 45 c.c. of water and 15 c.c. of HNO_3, filter and proceed as in the case of steels. It may be necessary to examine the residue for manganese.

For manganese ores proceed as above except to dilute to the mark in a calibrated flask, shake well and take an aliquot part equal to 1 per cent. of manganese on a 1 gram sample. However, the Volhard process is more especially adapted to high manganese ores.

References:

Blair, "Analysis of Iron and Steel," 7th edition, p. 121.

Demorest, "The Bismuthate Method for Manganese," *J. Ind. Eng. Chem.*, IV, Jan., 1912.

Blum, *J. Am. Chem. Soc.*, 26, 793.

Color Process for Manganese

When a solution of manganese in dilute HNO_3 is boiled with PbO_2 permanganic acid is formed, coloring the solution purple.

The depth of this color increases with the amount of manganese present, and by comparing it with that produced in the same way in a solution containing a known amount of manganese, that present in the first solution can be estimated. The method is sufficiently accurate for technical purposes, and can be applied to steels, pig-irons, and ores, in which the per cent. of manganese is small.

A standard is required containing a known amount of manganese. This standard should be of precisely the same kind of material as that to be analyzed; steel being used for steel, iron for iron, ore for ore, etc.

The PbO_2 must be free from manganese. It must be light brown in color, not dark brown as the dark variety gives low results.

While the method is most commonly applied to steel, it is applicable with slight modifications to the other materials mentioned.

As the depth and shade of color produced is influenced by the time of heating, the strength of the acid, and the volume of the liquid, it is essential that the standard and the sample be treated in exactly the same manner, and that the standard be near the sample in percentage of manganese. The process can be conducted in test-tubes or in small flasks. The boiling should be gentle but continuous, and so regulated as to cause equal concentration of the liquid in standard and sample.

Process for Steel.—Weigh 0.2 gram of the steel in a 50 c.c. Erlenmeyer flask. Add 15 c.c. of HNO_3, sp. gr. 1.2. Close the mouth of the flask with a small glass bulb; heat carefully on a hot plate or steam-bath until the iron is all dissolved. Transfer to a 100 c.c. graduated flask, filtering, if necessary, and dilute to 100 c.c. Mix thoroughly. Now put 10 c.c. of the solution into a small flask, add 3 c.c. of HNO_3, sp. gr. 1.2, and heat carefully on a hot plate. As soon as the solution is hot, but before it begins to boil, drop in a very little PbO_2, and when the solution begins to boil, add 0.5 gram more PbO_2. Close the flask with the bulb and keep the solution boiling gently but continuously for exactly five minutes. Now set the flask in cold water until the PbO_2 settles to the bottom and the violet liquid is absolutely clear. Avoid exposure to bright light which may cause the color to change. A solution of the standard steel should be prepared and treated in the same way and at the same time.

Pour off the two solutions into two graduated tubes and dilute the darker till the colors match when compared over a sheet of white paper. The volumes will then have the same ratio as the amount of manganese in the standard and test sample.

Small flasks used in this way and kept closed with glass bulbs are as satisfactory as the special calcium chloride bath and test-tubes sometimes used. The heavy lead precipitate settles so completely to the bottom that with care the liquid can nearly all be poured off without disturbing it. Where the standard and the sample are close in manganese content, the small amount of liquid left in each flask will not appreciably affect the results if the original volumes were about equal. Eight-inch test-tubes may be used instead of the flasks. They can be heated in a calcium chloride bath at 115°C., or on a sand-bath provided with a wire rack for holding the tubes.

The PbO_2 settles a little better in the tubes, which should be placed upright in cold water. If a centrifugal machine is available (such for instance as is used for separating the phosphorus precipitate for measuring in the Goetz process), the PbO_2 can be rapidly separated by pouring the contents of the flasks into test-tubes and whirling them in the machine.

The addition of a little PbO_2 before the boiling commences causes this to start off quietly, and on adding the rest of the reagent there is no violent action such as is likely to take place if the oxide is added at once to the boiling liquid and which may throw liquid out of the flask.

When the manganese is very low, 25 c.c. or more of the solution of the steel may be used instead of the 10 c.c. directed, provided the amount of HNO_3 is proportionately increased.

Dilution and division of the solution as directed is desirable, where the amount of manganese is sufficient to give a deep color. It is unnecessary in low manganese steel. In this case proceed as follows:

Dissolve 0.2 gram of the steel in 15 c.c. HNO_3, 1.2 sp. gr. Boil till nitrous fumes are expelled and add 15 c.c. of water, then add the PbO_2 and boil as before directed. Allow to settle, decant off, cool, and compare. Use care to heat the standard and sample equally, both during the solution and after adding the PbO_2. Instead of dissolving the standard each time a test is made, a quantity may be dissolved and the solution then diluted so that 10 c.c. corresponds to the weight of the sample taken in the test. This volume may then be taken for comparison with each set of tests. Thus for the first process where the solution is diluted and divided, dissolve 2 grams of the standard steel, dilute to 1 liter and use 10 c.c. each time for comparison.

For steels of moderate percentage of manganese the time of boiling may be shortened to three minutes.

Process for Pig-iron.—Dissolve 0.2 gram in 10 c.c. HNO_3, sp. gr. 1.2. Add ½ c.c. HCl and boil down to 1 or 2 c.c. Add 10 c.c. concentrated HNO_3 and boil down one-half. Now dilute to 100 c.c., filter through a dry filter, take an aliquot part of the filtrate and proceed as in the regular process. Use a pig-iron standard. With very low manganese or coarse-grained iron it may be desirable to take larger amounts to secure an average.

In this case use 1 gram and dilute to 100 or 500 c.c. according to the amount of manganese present.

Process for Ores.—Dissolve 0.2 gram in 5 c.c. of HCl. Boil down to a syrup; add 10 c.c. of concentrated HNO_3, evaporate again to a syrup. Add 10 c.c. of HNO_3, 1.2 sp. gr., dilute, filter and proceed as with pig-iron, using an ore standard.

References:
Hunt, *Trans.* Am. Inst. Mining Eng., XV, p. 164.

Lead Peroxide-arsenite Method

Instead of determining the manganese by comparing the colors in the above method, the permanganate may be titrated by a standard reducing agent, preferably arsenite because of its keeping qualities. The writer prefers to use bismuthate rather than PbO_2 because of its more certain oxidizing power, but the PbO_2 is cheaper.

Process.—Proceed exactly as directed above but instead of decanting from the lead peroxide, filter and wash twice. Now titrate with the arsenite as directed in the bismuthate-arsenite process.

Color Method using Ammonium Persulfate

This method is due to Marshal and Walters. It depends upon the fact that if ammonium persulfate (NH_4SO_4) is added to a solution of manganese in dilute nitric or sulfuric acid, it will, on warming, promptly and completely oxidize the manganese to permanganic acid, provided a small amount of silver nitrate is present. The silver salt is essential, for if not present the manganese will be precipitated as MnO_2. If too much silver salt is present, silver peroxide will precipitate and make the solution muddy.

The solution should not be boiled, but merely warmed until the color develops.

It is said that the persulfate should be slightly damp, but we have used this salt dried in a desiccator with satisfactory results.

Walter's Process for Steel.—Dissolve 0.1 or 0.2 gram of the steel, according to the percentage of manganese, in 10 c.c. of HNO_3, sp. gr. 1.2. Heat until all nitrous fumes are driven off. Now add 15 c.c. of a solution of silver nitrate containing 1.33 gram of the salt to 1 liter of water. This will cool the solution considerably. Now immediately add about 1 gram of ammonium

persulfate, and warm until the color commences to develop, and then for about a half minute longer. Remove from the heat and set it in cold water while the evolution of oxygen continues. As soon as the solution is cool, compare it with a solution of standard steel treated in the same manner.

The solution of the standard steel may be prepared in quantity, as noted before, by dissolving several grams of the metal in a sufficient amount of nitric acid, sp. gr. 1.2, and diluting with the same strength acid until 10 c.c. of the solution contain 0.2 gram of steel. Ten cubic centimeters of this solution are then used with each set of determinations.

Reference:

Chemical News, Feb. 15 and Nov. 15, 1911.

CHAPTER VII

THE DETERMINATION OF SULFUR

Sulfur occurs in iron ores as sulfides, such as pyrite (FeS_2) and sphalerite (ZnS) and also as sulfates, such as gypsum ($CaSO_4$, $2H_2O$), barite ($BaSO_4$) and celestite ($SrSO_4$). In iron and steel it occurs as sulfide only. In the gravimetric methods for determining sulfur it is first converted into some soluble sulfate and then the sulfuric acid precipitated by barium chloride and weighed as barium sulfate.

Direct Oxidation Methods

Conversion of the Sulfides to Sulfates.—All sulfides are completely oxidized to sulfates when fused with a mixture of dry Na_2CO_3 and $NaNO_3$ or with Na_2O_2.

As free sulfur and certain disulfides give off sulfur vapor at a comparatively low temperature (below the fusing-point of Na_2CO_3), when these are present care must be taken to prevent loss by the escape of this vapor. The mixture of ore and flux must be covered with a layer of the pure "fusion mixture" and heated carefully.

After fusion all the sulfur, whether originally present as sulfide or sulfate (even in $BaSO_4$) will be found as Na_2SO_4, the bases present remaining as oxides or carbonates. When the fused mass is boiled with water till thoroughly disintegrated and then filtered off and washed, the sulfate all passes into the filtrate.

Sulfides can be more or less completely oxidized to sulfates in the "wet way" by treating them with hot concentrated HNO_3 or aqua regia. Wet methods are not very satisfactory, as free sulfur is liable to separate and fuse to globules, its melting-point being below the boiling-point of HNO_3. Once in this form it is very slowly oxidized by boiling with ordinary oxidizing agents. Iron sulfide can be completely oxidized, however, by heating with a large excess of concentrated HNO_3 and adding a little powdered $KClO_3$.

When iron sulfide, or even iron containing but little sulfur, is dissolved in dilute HNO_3, 1.2 sp. gr., a considerable proportion of the sulfur separates as such and escapes oxidation.

Solutions containing ferric sulfate, on evaporation to dryness and

"baking," as is common in iron analysis, may lose SO_3 unless enough potassium or sodium is added to hold it all in combination with the alkali, as the sulfate of iron is easily decomposed by heat and SO_3 expelled.

References:

See Fresenius, "Quantitative Analysis;" also Phillips, *J. Am. Chem. Soc.*, 1896, p. 1079.

The Precipitation of the SO_3 by $BaCl_2$

This precipitation must be conducted under carefully regulated conditions, if the results are to be satisfactory.

When the amount of sulfur present is very small the contamination of the $BaSO_4$ is not apt to be important and the chief thing is to get the sulfur completely precipitated; but when large amounts of sulfur are to be precipitated, as when pyrite is to be analyzed, the case is very different and great care must be taken to have the $BaSO_4$ pure as well as completely precipitated.

When alkalies are present, all $BaSO_4$ precipitates carry down alkali sulfates, the error being worst if alkali chlorides are present. If ammonium salts are present, ammonium sulfate is carried down, and is of course lost on ignition. In the presence of much alkali chloride, the precipitate contains a certain amount of free sulfuric acid. All of these errors make results run low, in some cases perhaps as much as several per cent. of the total weight.

In addition to these minus errors, there are plus errors. All barium sulfate precipitates contain barium chloride. If the precipitation is made very slowly, the amount of this is very small. When the precipitation is made rapidly, it is much larger. Nitrates are occluded by barium sulfate, giving results which are high. When barium sulfate is precipitated from solutions containing much ferric iron, iron salts will adhere to the precipitate, making it reddish in color, unless considerable HCl is present. Some of the sulfuric acid appears to be in combination with the iron instead of with the barium, and is driven off on ignition, causing low results. Water alone will not wash out any of the above salts occluded with the barium sulfate.

Barium sulfate while very insoluble in water is not so in dilute acids, the amount dissolved increasing with the concentration of the acid, though the presence of a considerable excess of $BaCl_2$ very largely decreases the solubility of the barium sulfate in HCl. Acid solutions of $FeCl_3$, when hot, hold a little $BaSO_4$ in solution, which separates when the liquid cools.

The precipitate of $BaSO_4$ is fine, liable to run through the filter paper,

if precipitated cold, and so should be precipitated hot and allowed to stand on a warm plate with frequent stirring. In this way the precipitate will grow dense and granular so that it can be easily filtered.

It will be seen from the above that the determination of sulfur when present in large amounts is attended with many difficulties and for accurate results correction must be made by analysis of the precipitate. For good technical results perhaps the best way is to wash the precipitate off the filter back into the beaker, add HCl equal to the water present and evaporate almost to dryness, add 100 c.c. of water and 5 c.c. of 10 per cent. $BaCl_2$, let settle and filter.

References:

Hillebrand, *Bulletin* 422, U. S. Geol. Survey, p. 195.
Allen and Johnson, *J. Am. Chem. Soc.*, May, 1910, p. 588.
Archbutt, *J. Soc. Chem. Ind.*, IX, p. 25.
Lunge, *J. Soc. Chem. Ind.*, VIII, pp. 967 and 819.
Auchy, *J. Am. Chem. Soc.*, 1901, p. 147; *Am. Chem. J.*, 1902, p. 495.

Process for Sulfur in Iron Ores.—Mix 1 gram of the finely pulverized ore with 5 grams of dry Na_2CO_3 and 0.5 to 1 gram of $NaNO_3$, according to the amount of sulfur in the ore. Put the mixture in a platinum crucible and fuse carefully. As soon as it is well melted, chill the crucible by dipping the bottom into water. This will usually loosen the cake so that it can be removed from the crucible.

As ordinary gas contains sulfur, fusions made over it are likely to absorb some SO_2 from the flame. Therefore an alcohol or gasoline blast lamp should be used. If gas is used, the crucible must be kept covered during the fusion and should be protected by inserting it into a tightly fitting collar of sheet asbestos nearly to the top. This will act as a shield to prevent the products of combustion from getting into the crucible. In accurate work it is always necessary to make a blank analysis and determine the small amount of sulfur contained in the reagents or absorbed from the gas flames. Deduct this from the amount found when working on the ore.

Boil out the fusion with water until all the material is soft and no hard lumps remain. If the solution is colored by Na_2MnO_4, add a few drops of alcohol. Filter and wash well with hot water. Add HCl to the cold solution which should have a volume of about 100 c.c. The acid should be added until the solution is just acid, then about 4 c.c. more. Now heat nearly to boiling

and add 5 to 10 c.c. of a 10 per cent. solution of $BaCl_2$ previously diluted with 10 to 20 c.c. of water and heated. Stir and let the precipitate of $BaSO_4$ settle. When clear, filter, wash with hot water, ignite and weigh the $BaSO_4$. This weight multiplied by 0.1374 gives the amount of S.

If it is suspected that the $BaSO_4$ is contaminated with SiO_2 it should be treated with HF. It is a good thing to do in any case. Add to the ignited precipitate a drop of H_2SO_4 and 2 c.c. of HF. Evaporate off the acids and finally again ignite and weigh.

Notes on the Process.—$BaSO_4$ is easily reduced to BaS by heating with carbon. This may occur in the crucible and will make the results come low; hence, in igniting the precipitate detach it as far as possible from the filter, burn the paper carefully on a platinum wire, avoiding a high heat. Add the ash to the precipitate in the crucible and heat gently with the cover off until all the carbon is burned, finally igniting to a bright red heat.

Instead of drying the paper, the wet filter and precipitate may be ignited together by proceeding as follows: Put the filter paper containing the precipitate into a good-sized platinum crucible. The paper should be put in point down and open, just as it sets in the funnel. Now set the uncovered crucible over a very low flame and dry out the paper carefully. Then continue the heating to char the paper without letting it ignite. Should it catch fire, extinguish the flame by momentarily covering the crucible. When all the volatile matter is expelled, slightly increase the heat which should not, however, exceed a dull red. The carbon will now all burn away and the precipitate become white. Finally raise the temperature to bright redness. Cool and weigh as before. This process is called "smoking off" the filter and saves much time. It can be used safely on all small $BaSO_4$ precipitates. After weighing the precipitate, add a little water to it and test with turmeric paper. If it reacts alkaline, the results are untrustworthy, as reduction has occurred; in this case add a drop of H_2SO_4; heat till dry, ignite and weigh again, taking the second weight as the correct one.

Wet Oxidation Method for Sulfur in Ores

This method fails to determine the sulfur in any $BaSO_4$ or $PbSO_4$ contained in the ore. Therefore it is not so generally applicable as the fusion method unless the residue is separately treated by the fusion method and any sulfur thus obtained added to that obtained by the wet method.

Process of Analyses.—Weigh 1 to 5 grams of the very finely pulverized ore. Put it in a covered casserole or beaker and add 20 c.c. of concentrated HNO_3. Heat and add 1 gram of $KClO_3$ in several portions. Now digest at a moderate heat till all action ceases, then evaporate off most of the HNO_3. Add an excess of HCl and warm until the iron is all dissolved. Evaporate to dryness and proceed as with the dried residue in the determination of sulfur in iron or steel.

When sulfur is present in large amounts, as for instance, in pyrite, it is necessary that the $BaSO_4$ be precipitated from a solution free from iron. Dissolve 0.5 gram of the very finely ground sample in 20 c.c. of aqua regia in a beaker with a watch-glass cover. Heat until decomposition is complete, then evaporate to dryness. If necessary use a little $KClO_3$ with the aqua regia to dissolve the pyrite. Moisten the dry mass with 1 c.c. HCl and 100 c.c. of water. Heat until all except the gangue is dissolved and filter. To the *cold* solution add ammonia until alkaline, heat to boiling and filter off the $Fe(OH)_3$ and wash thoroughly. Make the filtrate acid with HCl, heat to boiling and add slowly $BaCl_2$ with constant stirring. After standing some time, filter and wash, transfer the $BaSO_4$ back to the beaker, add as much HCl as there is water present, evaporate almost to dryness, add 100 c.c. water and then 20 c.c. $BaCl_2$, allow to stand a half hour, filter and wash. Ignite very carefully to prevent reduction of the $BaSO_4$.

Method for Sulfur in Iron and Steel

As the sulfur is usually present in these metals in very small percentages only, its accurate determination demands great care.

Process of Analysis.—Take from 2 to 5 grams according to the percentage of sulfur. Add 25 to 40 c.c. concentrated HNO_3. Cool the dish if the action is too rapid, or heat it if it is too slow. The rate of solution must not be too rapid or low results may follow.

When the metal is nearly all dissolved, heat to boiling and add 2 to 3 c.c. of concentrated HCl to complete the solution. Now add about 0.5 gram $KClO_3$ free from sulfur. Boil to dryness and bake on a hot plate 10 minutes. Add 10 to 20 c.c. con-

centrated HCl to dissolve the residue and again dry down thoroughly. Dissolve again in 15 to 40 c.c. of concentrated HCl. Evaporate the solution until a skin begins to form on the surface or until it becomes syrupy. Now add 5 to 10 c.c. of concentrated HCl, according to the amount of iron taken. When all the iron dissolves dilute the liquid with its own volume of hot water and filter into a small beaker through a paper previously washed out with a little hot dilute HCl (this facilitates filtration). Wash the dish and insoluble residue with hot water.

The filtrate and washings must not exceed 75 c.c. Now warm to about 60°C. and add 10 c.c. of a 10 per cent. solution of $BaCl_2$. Let stand till the precipitate settles, leaving the liquid perfectly clear. (Two hours is sufficient if everything is right.)

Filter onto a small ashless filter, wash with water containing a few drops of HCl, ignite and weigh the $BaSO_4$. Test the filtrate by the addition of considerably more $BaCl_2$ solution which must give no additional precipitate.

The residue from which the solution for the determination of sulfur is filtered must contain no basic iron salts, as these may hold sulfur. These are likely to form if the HCl solution is concentrated too far and insufficient acid is added before dilution.

Reference:

J. Anal. and App. Chem., VI, p. 318.

Notes on the Process.—It is imperatively necessary that a blank be run on all the reagents used in the process and the weight of a $BaSO_4$ obtained in this way deducted from that found in the analysis.

Certain high carbon steels and most ferro-silicons will resist the action of concentrated HNO_3 almost entirely. When treating such metals add some potassium chlorate with the nitric acid at the start, and also at intervals add concentrated HCl, 1 c.c. at a time, until the metal is dissolved; then add more $KClO_3$ and proceed as usual.

Ferro-silicons with over 10 per cent. of silicon will resist the action of all the ordinary solvents. These and other insoluble alloys cannot be treated by wet methods for the determination of sulfur.

Where the percentage of silicon does not exceed about 15 per cent., the small addition of sodium fluoride to the HNO_3 as described under Phosphorus on page 46, will usually bring the metal into solution and the determination can then be carried out as usual, by adding the chlorate, evaporating, baking and taking up in HCl. In other cases the metal must be fused. The fusion is best made in a platinum crucible with a

mixture of equal parts of $NaNO_3$ and Na_2CO_3 using at least six parts of the mixture to one of the metal. The fusion can be then soaked out with water and the water solution treated as in the case of an ore.

The sulfur will all go into the water solution, provided the iron is completely oxidized. It is essential that the metal be very finely powdered. The peroxide of sodium can be substituted for the nitrate or may be used alone, in which case at least 8 grams of the reagent must be used for one of metal, and the fusion made in a nickel crucible. Blanks must be run on all the reagents.

References:

F. C. Phillips, *J. Am. Chem. Soc.*, 1896, p. 1079.

E. H. Saniter, *J. Soc. Chem. Ind.*, 1896, p. 155.

The Determination of Sulfur in Pig-iron and Steel by Evolution as H_2S

The direct oxidation methods are accurate and the only ones that can be relied upon to give with certainty the total sulfur in any material. But they are too slow to answer for control work. For such purposes the evolution methods are very generally used. They are either gravimetric or volumetric and can be made extremely rapid. For some materials they will give reliable results.

These methods all depend upon the assumption that when iron is dissolved in HCl the whole of the S is evolved as H_2S and passes off with the excess of hydrogen. This is probably true or nearly so for steel containing but little carbon and possibly for gray pig-iron; it certainly is not true for white iron and mottled irons high in combined carbon; and probably not true for high-carbon steels and some ferro-silicons, especially those containing much sulfur.

In these latter materials part of the sulfur appears to be evolved as more or less volatile liquid or possibly gaseous compounds of carbon, hydrogen and sulfur and not as H_2S. The proportion of the sulfur evolved as H_2S will vary in the same iron if the heat treatment has been different; if slowly cooled, it may be gray and evolve most of the sulfur as H_2S; if suddenly cooled by chilling in water (shot samples) it will be white and only a small portion of its sulfur may be evolved as H_2S. Hence by evolution methods the latter sample would show a much lower percentage of sulfur than the former. The sulfur that is lost is in the form of $(CH_3)_2S$ or some similar form. The higher the percentage of carbon in solid solution (Martensite) in the iron the more sulfur is thus lost. Part of this goes over with the gases and part stays behind in the flask. If the evolved gases be passed with hydrogen through a glass

tube heated to dull redness the sulfur compounds are changed to H_2S. If the tube is filled with asbestos coated with platinum black the action is more rapid. Care must be taken to exclude air or explosion will result. The amount of sulfur evolved in combination as $(CH_3)_2S$ increases with the manganese in the sample and decreases with the phosphorus. Of that retained in the flask, part may be in this form and if any titanium is present some will be held in combination with the titanium. Phillips has shown that sulfur retained in the flask as difficultly volatile organic compounds may be distilled off by prolonged boiling.

By taking certain precautions the amount of sulfur lost can be reduced to a very small amount and the results by the evolution process can be made to check fairly well with the standard process even on pig-irons. These precautions are as follows:

(1) The weighed sample should be annealed in a non-oxidizing atmosphere according to a certain procedure. This changes the martensite to pearlite with cementite, graphite or ferrite according to the amount of carbon. (2) The speed of solution should be as great as possible. (3) The acid used should be concentrated acid, of sp. gr. 1.19. Under these conditions the use of a hot tube through which to pass the evolved gases is not necessary.

Ordinary low-carbon steels do not have to be annealed, but high-carbon steels, pig-irons and the alloy steels, such as self-hardening steels and nickel-chromium steels must be annealed to get correct results.

For rapid work, as for furnace control, the annealing of the sample may be omitted but it should be understood that this always gives low results, sometimes as much as 20 per cent. low, when the sample is a pig-iron.

On the other hand, in the case of steels, the results for sulfur by the evolution process may give too high results. Besides H_2S other gases are given off which may affect the results. These are hydrocarbons and PH_3 and AsH_3 which are absorbed to a certain extent and affect iodine used for titrating, but do not affect gravimetric results. According to Elliot these are not absorbed in $CdCl_2$ solution containing acetic acid and ammonium acetate as they are in alkaline solutions or in solutions of lead, zinc, or copper.

The H_2S evolved is very easily decomposed by comparatively feeble oxidizing agents, water being formed and free sulfur deposited. *Prolonged* contact with air and sunlight, the presence of $FeCl_3$, traces of chlorine, all act on it in this way, and must be avoided in the process. There is no necessity, however, of working in an atmosphere of hydrogen or of carbon dioxide if the process is *rapidly conducted*. On the other hand, slow evolution, or the use of HCl containing traces of chlorine or $FeCl_3$ will cause decomposition of the H_2S and retention of sulfur in the residue.

Rusting of the drillings previous to the addition of HCl leads to the formation of $FeCl_3$ and may cause a separation of sulfur from the gas in the flask. Dilute HCl (1 : 1) is usually used in these methods but according to the writer's experience this sometimes fails to cause complete evolution of the sulfur as H_2S where the concentrated acid succeeds. (See PHILLIPS, J. Am. Chem. Soc., 1895, p. 891.)

While the H_2S is easily absorbed, the organic sulfur compounds are only slowly and incompletely taken up. Long boiling is frequently necessary to drive them completely out of the flask in which the iron is dissolved. It is evident from what has been said that the evolution processes are reliable only when they are checked by using the gravimetric process on the same kind of sample.

The H_2S evolved may be determined in many ways. It may be absorbed in an alkaline solution of lead acetate, then oxidized to SO_3 and precipitated by $BaCl_2$, or it may be absorbed in a solution of HCl and bromine and the H_2SO_4 formed precipitated by $BaCl_2$, or in an alkaline solution of $KMnO_4$ and precipitated as before. Some chemists absorb the H_2S in a $CuSO_4$ solution, filter off the copper sulfide, ignite and weigh as CuO. The most widely used method is, however, a volumetric one in which the H_2S is titrated with a standard iodine solution. It is very rapid and is quite as accurate as the other evolution methods.

THE IODINE METHOD FOR SULFUR

The H_2S may be absorbed in NaOH or KOH or an ammoniacal solution of zinc or cadmium. The cadmium solution is preferred because it fixes the sulfur in a visible form and is not easily altered on standing. KOH and NaOH are liable to contain oxidizing impurities such as nitrites or ferric hydroxide which would oxidize H_2S.

The reactions involved in the process are as follows:

$$FeS(\text{or } MnS) + 2HCl = FeCl_2(\text{or } MnCl_2) + H_2S.$$
$$H_2S + CdCl_2 = CdS + 2HCl.$$

The HCl liberated is neutralized by the NH_4OH present. When the H_2S has all come over, the solution is diluted and strong HCl is added in excess; then the reverse reaction takes place,

$$CdS + 2HCl = H_2S + CdCl_2.$$

A considerable excess of HCl is necessary to completely dissolve all of the CdS. The volume of the solution should be very large to prevent the escape of the liberated H_2S. Also it should *not* be *hot*.

The H_2S is then titrated with iodine.

$$H_2S + 2I = 2HI + S.$$

The liberated sulfur causes the liquid to become curiously opalescent and show various colors, but this does not at all obscure the end reaction which is very sharp. Before titration a little starch solution is added to the liquid to be titrated. One drop of iodine in excess of the amount required to titrate the H_2S causes an intense blue color of "starch iodide" to be formed.

Preparation of the Starch Solution.—Stir 5 grams of starch into 200 c.c. of cold water. Heat the liquid to boiling with constant stirring until the starch is thoroughly dissolved. Now dilute the liquid with cold water to about a liter, and add 10 grams of crystallized $ZnCl_2$. Let the solution settle for some time, and pour off for use the nearly clear supernatant liquid. This solution is very sensitive and keeps indefinitely.

A solution of 1 gram of starch in 200 c.c. of boiling water alone may be used, but it must be made fresh every day.

For a more sensitive preparation of starch see page 225.

Preparation of the Iodine Solution.—Weigh on a watch-glass 3.96 grams of pure resublimed iodine. Put it into a liter flask, add about 6 grams of pure potassium iodide (free from iodate) and 10 c.c. of water. Let stand in the cold until all the iodine dissolves. Then dilute to 1 liter.

One cubic centimeter of this solution should be equivalent to 0.0005 gram of sulfur. If 5 grams of metal are taken for the analysis each cubic centimeter of iodine solution consumed will be equivalent to 0.01 per cent. of sulfur.

In the reaction $H_2S+2I=2HI+S$, two atoms of I are equivalent to one atom of S, or 253.84 grams of $I=32.06$ grams of S. To find the amount of I, which must be contained in 1 c.c. to give a solution of the above value in sulfur, make the proportion $0.005 : x = 32.06 : 253.84$. This gives $x = 0.003957$ gram per 1 c.c. or 3.96 grams per liter.

Iodine is insoluble in water, but is easily and rapidly dissolved in *a very concentrated* solution of KI, though very slowly in a dilute one.

The iodine solution is not constant; hence, its strength must be determined frequently.

Standardizing the Iodine Solution.—Prepare the following solutions:

A. Eight grams crystallized sodium thiosulfate dissolved in water and diluted to 1 liter.

B. 0.1531 gram of fused potassium dichromate is dissolved in water and diluted to 100 c.c. If more convenient this solution may be made by diluting 10 c.c. of the dichromate solution used in the iron assay (of which 1 c.c. equals 0.01 Fe) to 57.42 c.c.; 10 c.c. of this solution will liberate iodine from KI equivalent to 0.005 gram sulfur.

Measure with a pipette 10 c.c. of the thiosulfate solution A into a beaker. Add 100 c.c. of water and 1 c.c. of starch solution. Now run in the iodine solution from a burette until the last drop gives a decided blue color not disappearing on stirring. Note exactly the amount used. Repeat the determination two or three times (the results should agree almost exactly), and take the average as the amount of iodine solution equivalent to 10 c.c. of the thiosulfate.

Measure 10 c.c. of the dichromate solution B into a beaker. Add 50 c.c. of cold water and then about 0.5 gram of pure KI. When the KI is dissolved add 5 c.c. of concentrated HCl.

The KI must be free from iodate. It may be tested by dissolving a portion in water, adding some starch solution and a little HCl. The liquid should not show more than a trace of blue color and should become absolutely colorless on the addition of a small drop of the thiosulfate solution. The acid must be free from chlorine or ferric chloride. When diluted it should give no blue color on the addition of KI and starch.

Let the mixture stand six or seven minutes without warming (which would volatilize iodine). Dilute to 100 c.c. and add 10 c.c. of solution A and 1 c.c. of starch solution. Should this color the liquid blue, add 10 c.c. more of the thiosulfate solution which will make it colorless. The first 10 c.c. is usually sufficient. Now *immediately* titrate the excess of thiosulfate with the iodine solution, adding it till the blue color is developed. Note exactly the volume of the solution used; call it R.

It is important that there be no delay between the addition of the solution "A" and the iodine titration on account of the presence of free HCl in the liquid. Thiosulfate is slowly decomposed by HCl with the separation of sulfur and the formation of H_2SO_3 which absorbs twice as much iodine.

By keeping the excess of thiosulfate small and titrating it within one minute, correct results can be obtained.

Now the difference between "R" and the number of cubic centimeters of the iodine solution that are equivalent to the number of cubic centimeters of the thiosulfate solution "A" added to the dichromate and iodide as above, is the volume of the iodine solution that is equivalent to 0.005 gram sulfur, and 0.005 divided by this difference is the value in sulfur of 1 c.c. of the iodine solution. This is the factor by which to multiply the number of cubic centimeters taken in the analysis in order to obtain the amount of sulfur present.

Example.—Suppose 10 c.c. of solution "A" equals 10.6 c.c. iodine solution. Second, that 20 c.c. of "A" were added to the 10 c.c. of "B" and the KI, and that the mixture required 9.8 c.c. of iodine solution on the titration back; that is, "R" equals 9.8. As the 20 c.c. of "A" alone would equal 21.2 c.c. of iodine, we have 21.2 − 9.8 = 11.4, which is the number of cubic centimeters of iodine solution equivalent to 0.005 of sulfur, because this is the sulfur equivalent to the iodine that is liberated from the KI by the dichromate. Further, 0.005 divided by 11.4 equals 0.000439, which is the amount of sulfur to which 1 c.c. of the iodine solution is equivalent.

The reactions upon which this process of standardizing depend are:

1. $2Na_2S_2O_3\ 5H_2O+2I=2NaI+Na_2S_4O_6+5H_2O$. (The crystallized thiosulfate contains five molecules of water.)

2. $K_2Cr_2O_7+6KI+14HCl=8KCl+2CrCl_2+7H_2O+6I$.

Two molecules of thiosulfate weigh 496.64, and as two molecules of thiosulfate are equivalent to two atoms of iodine (253.7) we have the proportion 496.64 : 253.7 = 7.75 : 3.975, 7.75 being the amount of thiosulfate which should be dissolved in 1 liter to give a solution equivalent to the iodine, but as it is desirable that this solution be a little stronger, 8 grams are actually taken.

The thiosulfate solution is not constant, hence cannot be used as an absolute check on the iodine solution, but only as a means of comparing it with an absolutely known amount of iodine. This definite amount of iodine is obtained from the action of dichromate on an excess of KI in the presence of HCl. The reaction between KI and $K_2Cr_2O_7$ is not instantaneous, but rapidly becomes complete.

The relation between the $K_2Cr_2O_7$ and the I is 294.2 : 761.5, hence 0.01531 $K_2Cr_2O_7$ will liberate 0.0396 gram of iodine, the amount which should be present in 10 c.c. of the iodine solution if its strength were exactly right.

The operation itself consists therefore in finding how much of the iodine solution to be standardized is required to titrate the amount of the thiosulfate solution which is equivalent to exactly 0.0396 gram of iodine, as liberated by the dichromate. Thus we find *first* how much of the iodine solution is equal to a certain amount of the thiosulfate solution; *second*, how much of the same iodine solution is equal to what is left after the same amount of thiosulfate has been acted upon by 0.0396 gram of iodine, and the difference is obviously the amount of iodine solution which contains 0.0396 gram of iodine, that is to say, will be equivalent to 0.005 of S; but this should be 10 c.c., hence the difference between 10 and the amount taken is the amount the solution is off the standard.

The only precautions to be noted are the necessity of giving *time* for the $K_2Cr_2O_7$ to react on the KI and the necessity of avoiding *heat* as iodine is readily volatilized from this solution.

The HCl used must be free from all impurities which liberate iodine from KI(Cl_2, $FeCl_3$, $CuCl_2$, etc.).

The iodine solution may also be standardized against a sample of iron or steel similar to that to be analyzed in which the sulfur has been accurately and repeatedly determined by the direct oxidation or nitric acid method.

Treat a given weight of the metal by the regular process and determine the volume of the iodine solution required to titrate the H_2S evolved. Then from the known sulfur percentage in the metal calculate the sulfur value of 1 c.c.

Make a factor of correction to apply to the iodine solution. This method of standardizing has the advantage of causing all errors of solution, evolution and oxidation to affect the standard and sample alike, and makes the evolution method give results comparable with the gravimetric method. It should always be used where a material of generally uniform character has to be tested as manufactured. As the heat treatment and the nature of the metal cause differences in the percentage of sulfur evolved as H_2S, an iodine solution standardized on metal should never be used for a metal made by a different process, as for example, one standardized on pig-iron for steel. (See Wilson, J. An. and App. Chem., V, 439.) When the sample is annealed the method of standardization does not make so much difference.

Cadmium Solution.—Dissolve 4 grams of cadmium chloride in 100 c.c. of water, and when dissolved add an equal volume of strong ammonia.

Apparatus.—This is shown in Fig. 4 and consists of a flask F

of 500 c.c. capacity and fitted with a rubber stopper, a glass-funnel tube G provided with a stop-cock, and a delivery tube H, in which are blown two or three good-sized bulbs. These bulbs serve to arrest the liquid condensing in the tube and allow it to return to the flask instead of working over into the absorption tubes. A water-cooled condenser is better. The delivery tube should carry the gas down to the bottom of a large test-tube I, 8 in. deep and 1¼ in. wide and fitted with a rubber stopper through which a second tube carries the gas into a second smaller test-tube J, which serves to catch any absorbable sulfur compounds escaping the first test-tube. This guard tube will rarely show any sulfur. Gas which is used to drive over the last trace of H_2S is introduced through G in the top of which is fitted a one-hole rubber stopper with a glass tube connected to a source of gas.

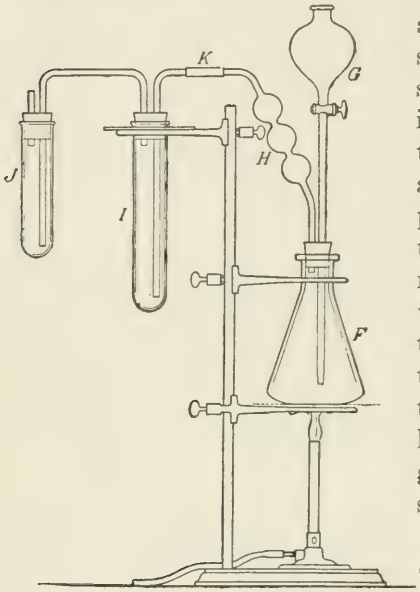

FIG. 4.

In place of the receiving cylinder or test-tube, some use a large flask, diluting the absorbing liquid correspondingly. The titration can then be made in the same flask without transferring the liquid. When the bubbles do not pass through a considerable depth of liquid, as when a flask is used as a receiving vessel, it is best to have the delivery tube in the vessel end in the form of a funnel to keep the gas longer in contact with the liquid.

Amount of Metal Taken.—This may be 5 grams for ordinary irons or 10 grams if the sulfur is very low. If the iodine solution is a little "off the standard"—that is, if 10 c.c. are equal to a little more or less than 0.005 gram sulfur—it is more convenient, instead of correcting each reading by multiplying it by the true sulfur value, to change the amount

of the sample taken so that 1 c.c. of the iodine solution shall represent 0.01 per cent. of sulfur.

For example: Suppose that the iodine solution is too weak and that 1 c.c. is only equal to 0.0004854 gram of sulfur instead of 0.0005 gram. In this case weigh out 4.854 grams of the metal for the determination. Then obviously each cubic centimeter of the iodine solution used in the titration will stand for 0.01 per cent. of sulfur, and the calculations which would be necessary if 5 grams had been taken will be avoided.

The foregoing method of applying the correction factor of a volumetric solution to the amount weighed out may be applied to any similar process; as, for example, in the determination of iron, phosphorus or manganese; and where many analyses are to be made will save much time as well as diminish the chances of error involved in the calculations.

Process for the Analysis.—Transfer the weighed metal to the flask and add about 2 grams of pure precipitated $CaCO_3$. Pour 5 c.c. of the cadmium solution into the absorbing tube and add to it 10 to 15 c.c. of strong NH_4OH. Now fill the tube with water to a depth of 6 in. Put 50 c.c. of HCl, sp. gr. 1.19, into the bulb of the funnel tube. Run in the acid slowly until the $CaCO_3$ is all dissolved, then run the acid in rapidly but avoid so rapid an evolution of gas as to throw the liquid out of the tube or make bubbles large enough to fill the tube. When the evolution of gas slows up, heat the flask hot enough to make the evolution of gas rapid, but do not boil until the iron is all dissolved as this would cause too much acid to distill over. When the iron is dissolved, boil the solution for several minutes. For the best results pass a stream of hydrogen or carbon dioxide or natural gas (purified by passing through NaOH solution) through the apparatus to drive out all traces of H_2S. The solution in the tube must be kept alkaline by adding more ammonia if necessary. The CdS should separate as a yellow precipitate. If it is pale in color, the sulfur is not being evolved properly as H_2S.

When using concentrated HCl, a considerable amount of acid distills over unless a water-cooled condenser is used, but by using sufficient NH_4OH, it will do no harm. After the liquid has been boiled several minutes and no more gas is coming over, open the stop-cock in the funnel tube, remove the lamp, and detach the delivery tube. Empty the absorbing tube into a large flask, wash it and the delivery tube well with water and pour the wash-

ings into the flask. Now add 300 or 400 c.c. of cold water, and then HCl enough to make the solution acid and 10 or 15 c.c. more, which should dissolve the precipitated CdS. Now add 1 c.c. of the starch solution and titrate immediately with the iodine solution, adding it until the last drop changes the opalescent liquid to a deep blue not disappearing on standing two or three minutes.

The number of cubic centimeters used, after correction for standard, will give the amount of sulfur in hundredths of a per cent. Always make a blank test on the reagents; they will usually consume a little iodine which must be deducted from that used in the analysis.

Notes on the Process.—Use pure gum-rubber tubing in the connections. White or red rubber may contain metallic sulfides evolving H_2S when acted upon by the HCl vapor, thus causing errors.

It is essential that the process be carried through promptly. There should be no delay in titrating. If the solution containing the CdS be allowed to stand it may lose H_2S or the sulfides may oxidize. This is especially important after the addition of HCl, as the free H_2S will oxidize very rapidly on standing. Zinc salts (acetate or sulfate) may be used in the place of cadmium with satisfactory results.

The Use of NaOH instead of $CdCl_2$.—The process is conducted as before, except that the absorption tube is filled with 80 c.c. of a 15 per cent. solution of NaOH. After the evolution of the gas, wash out the tube into a large beaker, dilute as before with cold water, acidify, add starch solution and titrate. Most caustic soda contains a little iron as ferric hydroxide, which dissolves in the concentrated solution but separates on dilution; hence, the 15 per cent. soda solution should be prepared some time before use, and the clear liquid decanted from the precipitate which usually settles. Test the solution also for nitrites and hypochlorites by acidifying a portion with HCl, and then adding KI and starch paste. It must show no blue color. In acidifying the soda solution before titration add a drop of phenolphthalein solution, and then add the HCl till the red color is discharged. The HCl must be pure. It will occasionally contain traces of SO_2 which would of course vitiate the results.

The cadmium method is sometimes modified by filtering off the CdS and putting the filter and precipitate into a large volume of water, adding HCl and titrating. This avoids the presence of a large amount of ammonium salts and of any hydrocarbons absorbed in the liquid. It has been claimed that these act slightly on the iodine. The advantage

of this modification is very slight if any, as the evolution process usually gives low results any way.

The method as above given is very rapid, but gives accurate results only on those samples which give up all their sulfur as H_2S. The following method, first proposed by Walters and Miller, and modified by many others, is the method elaborated by Elliot (J. Iron and Steel Inst., 1911, p. 412) and is good for all kinds of samples.

Annealing-evolution Process.—Five grams of the sample are mixed with 0.25 gram of pure finely powdered anhydrous potassium-ferrocyanide, and wrapped in one 11-cm. filter paper if the sample is a graphitic iron, or two papers if it is a steel or white iron, placed in a small porcelain crucible, covered with a lid, and annealed at 750° to 850°C. (just above the recalescence temperature) for 20 minutes in a muffle. The crucible is removed and allowed to cool slowly. The drillings should still be covered with charred paper. The drillings are now transferred to the evolution flask and the process continued as described for the evolution process above. Instead of using an alkaline cadmium chloride solution Elliot uses the following: 20 grams of $CdCl_2$ are dissolved in water and NH_4OH added until the $Cd(OH)_2$ dissolves. Then acetic acid is added until the liquid is acid, then 20 c.c. more. The solution is diluted to 1000 c.c. Fifty cubic centimeters are used for each determination. According to Elliot this solution does not dissolve hydrocarbons, phosphides, etc., as alkaline solutions do.

This process gives good results even on alloy steels and titaniferous pig-iron.

References on the Evolution Process:

Elliot, *J. Iron Steel Inst.*, 1911, p. 412.
Orthey, *Z. angew Chem.*, 1359–64, 1393–9.
Kinder, *Stahl u. Eisen*, XXVIII, 249–54.
Trans. Am. Inst. Mining Eng., X, 187 (cadmium), and XII, 507 (bromine).

Drown's Method with Potassium Permanganate

This is the least troublesome of the gravimetric evolution methods. It is accurate for those metals which evolve their sulfur as H_2S. The H_2S is absorbed by an alkaline solution of $KMnO_4$. This is a more energetic absorbent than the neutral solution originally proposed by

Dr. Drown, hence the gas can be sent through the liquid much more rapidly without danger of any sulfur escaping absorption.

As the rubber stoppers and tubes used in the apparatus may contain sulfur they must be kept from contact with the absorbing solution. They should be prepared for use by first boiling them for some time in a dilute solution of NaOH, then rubbing them well to remove any crust from the surface, and finally washing them thoroughly with water and dilute HCl.

Process of Analysis.—Weigh 5 or 10 grams of the drillings according to the percentage of sulfur contained in the metal, into the flask. Put into the first test-tube in the absorbing train 30 c.c. of a solution of potassium permanganate, 5 grams to the liter, and 30 c.c. of a 10 per cent. solution of pure sodium hydroxide. Charge the second tube in the same way, using half the amounts. Add water to the tubes until they are about half filled by the liquid; there should be a space of 3 or 4 in. above the liquid in each tube. Now connect up the apparatus, put 50 or 60 c.c. of concentrated HCl into the funnel tube, and cautiously run this into the flask. This should be done rapidly but not so as to cause such an evolution of gas as to form very large bubbles in the tubes, or to throw the absorbing liquid up against the corks. As the absorbing liquid is alkaline, the evolution of the gas can be quite rapid without danger of H_2S escaping absorption, and the more rapidly the iron is dissolved the larger the percentage of the sulfur which appears to be evolved in an absorbable form. When the action becomes slow and the iron is nearly all dissolved, bring the contents of the flask to boiling and boil until the liquid in the first tube grows quite warm and MnO_2 begins to separate. The steam will drive over all the H_2S and also to some extent carry over difficultly volatile sulfur compounds, leaving the residue in many cases practically free from sulfur. Now remove the lamp, being careful to immediately open the stop-cock of the funnel tube so as to admit air to the flask as it cools, or a vacuum may form and the contents of the test-tubes be drawn back into the flask.

Disconnect the test-tubes, empty them into separate beakers, washing out both the connecting tube and the test-tubes with water. Any MnO_2 adhering to the tubes should be dissolved off with a little HCl, and the solution added to the liquid from the test-tubes. A little oxalic acid should be added to the HCl so

used. The contents of the second tube should be alkaline at the end of the process though the HCl distilling over will probably have neutralized the alkali in the first tube and dissolved most of the MnO_2. Now heat the contents of the beakers, and if not already acid add a slight excess of HCl which may cause MnO_2 to separate. Drop in a solution of oxalic acid carefully until the MnO_2 is all dissolved and the solutions are colorless. Add to each beaker 15 c.c. of a 10 per cent. solution of $BaCl_2$, settle, filter, wash and weigh the $BaSO_4$ as usual. The liquid from the second tube should show no more than a trace of $BaSO_4$. Filter this in with the first precipitate. Should the second tube show much precipitate repeat the process, evolving the gas more slowly. Run a careful blank on the permanganate, soda, acids, etc., using the same amount of each as is taken in the analysis, and deduct the weight of the $BaSO_4$ found in this (due to impurity of reagents) from that found in the analysis.

Instead of using concentrated HCl in the process, many prefer to use the acid diluted with its own volume of water. It is easier to conduct the process in this way, as less of the acid distills over into the tubes, but it is a little more liable to leave sulfur behind in the residue.

Aspiration of air or CO_2 through the flask to remove the last traces of H_2S is unnecessary with the small percentages of sulfur found in iron and steel.

Examination of the Residue in the Flask for Sulfur.—Filter the contents of the flask through a 9-cm. filter, wash the residue thoroughly and dry it at a temperature not exceeding 100°C. Open out the filter and brush the residue into a small beaker. Add 10 c.c. of concentrated HNO_3 and a small crystal of $KClO_3$. Boil down to dryness, take up by heating with 5 c.c. of concentrated HCl, dilute to 30 or 40 c.c., filter and add 5 c.c. of $BaCl_2$ solution to the filtrate. Let stand till any precipitate of $BaSO_4$ settles, filter it off and weigh it.

The residue may also be treated by fusion exactly as an iron ore, of course using smaller quantities of fluxes.

References:

Drown, *Trans.* Am. Inst. Mining Eng., II, p. 224.

Auchy, *J. Am. Chem. Soc.*, 1896, p. 404.

Special Method for Sulfur in High-percentage Alloy Steels.—In these materials Müller and Diethelm determine the sulfur in connection with the direct combustion method for carbon. The steel is burned in an electric furnace at 1100°C. Following the combustion furnace but on the same tube is a second heating apparatus to heat the tube to 350°C. and in this part a couple of boats are placed to hold 8.5 grams of PbO_2. The sulfur is retained by the PbO_2 which is removed and boiled with Na_2CO_3. The sulfur is then determined in the solution by precipitating with $BaCl_2$ from an acid solution. See Z. angew. Chem., XXIII, 2114.

Sulfur in ferrovanadium cannot be determined by the evolution method; it must be determined by the gravimetric method. (Clark, Met. Chem. Eng., XI, 256.)

CHAPTER VIII

THE DETERMINATION OF CARBON IN PIG-IRON AND STEEL

The carbon in gray pig-iron occurs mostly as mechanically admixed graphite, with a small proportion as a carbide Fe_3C, called "Cementite." In white iron and chilled iron, as well as in steel, the carbon exists chiefly either as a carbide or in solid solution, forming the phase known as "Austensite" or its transition form called "Martensite." Malleable iron (made by prolonged annealing of white iron) contains carbon in a more finely divided form than graphite, but not in combination with iron.

When an iron containing carbon in these different conditions is dissolved in hot HCl or HNO_3, sp. gr. 1.2, the graphite and amorphous carbon are entirely left as a black residue which can be filtered off, while the combined carbon stays in solution entirely if HNO_3 is used, but passes off partly as hydrocarbon if HCl is used.

Methods are here given for the determination of "total carbon," "combined carbon" and "graphitic carbon."

Determination of Total Carbon

The total carbon is usually determined by one of the following methods:

A. Direct oxidation of the iron and carbon in some form of a furnace in a current of oxygen. The drillings may or may not be mixed with an oxidizing agent such as Pb_3O_4 in order to insure complete combustion, or with some flux to permit the oxygen to completely oxidize the iron.

The CO_2 liberated may be caught in an alkaline solution and weighed, or it may be precipitated as $BaCO_3$ which is filtered off and weighed, or it may be absorbed in an alkaline solution of known strength and the excess of alkali titrated by standard acid, or finally the CO_2 may be measured by gas volumetric methods. The last method is not widely used.

B. The iron is dissolved in a solvent, generally K_2CuCl_4, which leaves all the carbon, whether free or combined, undissolved. The carbon is filtered off on asbestos and burned to CO_2 and determined as above.

The burning or oxidation of the carbon may be done either in a furnace (including such devices as the Shimer crucible) or it may be done by a wet process, as by combustion in sulfuric and chromic acids.

C. Solution and simultaneous oxidation of the sample in sulfuric, chromic and phosphoric acids, the CO_2 being either measured or weighed.

D. When the carbon is present entirely as combined carbon as in steel it may be determined colorimetrically.

Direct Combustion Method for Carbon

This is the method most widely in use. When used with proper precaution it is very accurate and very rapid. A complete determination can be made in 25 minutes or less.

The complete combustion of steel drillings is dependent upon the temperature of the furnace. With sufficiently high temperature any ordinary steel can be completely burnt in a stream of oxygen without using red lead. The temperature ordinarily attainable, however, is not sufficient to burn completely such alloys as ferro-chrome, etc., and such samples must be mixed with red lead. Pig-iron also requires some red lead. The drillings should not be too coarse or combustion is apt to be incomplete. They should go through a 20-mesh sieve, although the writer has had no difficulty with coarser samples when the temperature of the furnace was 1050°C. Some chemists place the drillings in as compact a mass as possible in order that the heat of the burning iron may keep it at a high temperature. This will cause the mass to fuse unless the flow of oxygen is carefully regulated, and enclose particles of unburned iron and also destroy the boat. The writer prefers to scatter the drillings along the boat and then maintain a high enough temperature in the furnace to insure complete combustion. Some chemists mix the drillings with ignited alumina or Mn_3O_4 in order to keep the drillings separated.

Such alloys as ferro-chrome, ferro-molybdenum, ferro-tungsten and the "high speed steels" cannot be accurately analyzed for carbon by the methods involving solution in K_2CuCl_4 as hydrocarbons are evolved upon solution. So they must be analyzed by some form of direct combustion. (See Johnson, "Chemical Analysis of Special Steels, Steel Making Alloys and Graphites," p. 132 et seq.)

Apparatus Used.—Either gas-heated furnaces or electrically heated furnaces may be used. The writer prefers the electric furnace because of the ease with which the temperature may be controlled and because it does not heat up the laboratory noticeably. The bars on the rheostat are numbered and this apparatus

is calibrated so that each number corresponds to a certain temperature in the furnace. This avoids the continual use of a pyrometer. Fig. 5 shows the apparatus.

A is an oxygen tank which delivers oxygen at a constant pressure.

B is a silica tube containing palladiumized asbestos. It is heated with a wing top burner and burns any hydrocarbons contained in the oxygen. With good oxygen it may be omitted.

C is a bottle containing KOH solution.

D is a bottle tube containing sulfuric acid.

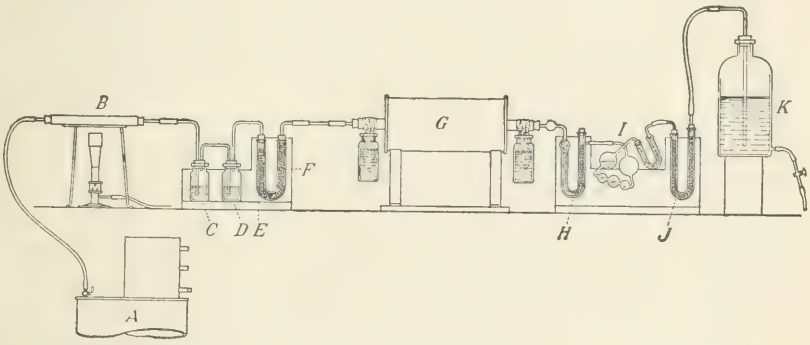

Fig. 5.

E-F is a "U" tube containing soda-lime (E) in one limb and $CaCl_2$ (F) in the other.

G is a Hoskin's electric furnace. The tube is of fused silica $\frac{7}{8}$ in. internal diameter. The tube is empty to the middle beyond which is a roll of CuO wrapped in asbestos paper, then a plug of palladiumized asbestos, then a boat containing $PbCrO_4$. The copper oxide and the palladiumized asbestos insure the combustion of any CO to CO_2. As a rule they are not needed but it is safest to use them in case of the combustion of pig-iron. CuO and $PbCrO_4$ must not be placed in contact with the silica tube as they will destroy it. [The $PbCrO_4$ is placed where the tube attains only a dull red heat; it must not be heated to the full heat of the furnace.] The CuO should be in the hot part of the furnace.

H is a "U" tube containing granular zinc in the left side and

$CaCl_2$ in the right. The zinc together with the $PbCrO_4$ remove the sulfur fumes resulting from burning the sample. The zinc also removes chlorine and litharge fumes. The $CaCl_2$ insures that the gas enters the weighing apparatus with the same degree of dryness as it leaves it. Otherwise it will gain or lose weight.

I is the weighing apparatus. There are many kinds, but the writer prefers a Liebig bulb to which is attached a 2 in. "U" tube containing soda lime in the side next to the KOH bulb and $CaCl_2$ in the other side with a plug of cotton separating them. The tubes at the entrance and the exit of the weighing apparatus should be softened until nearly closed. The gas should bubble through all the bulbs of the Liebig apparatus, then pass over the soda lime, then over the $CaCl_2$. See Fig. 9, page 127.

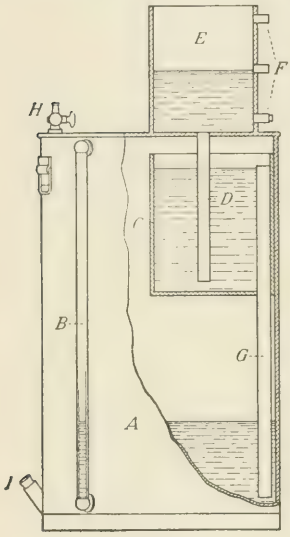

Fig. 6.

J is a guard tube containing $CaCl_2$ in the left side and soda lime in the right side.

K is an aspirator to draw the gas through and also to indicate how much has been aspirated.

The KOH used in the weighing apparatus is a 30 per cent. solution. It should be previously heated to boiling with a little $KMnO_4$ to oxidize the iron which it generally contains. Otherwise it will absorb oxygen during the aspiration and gain weight. The weighing bulbs should be washed off after they are filled and then wiped dry. If the entrance and exit tubes are nearly closed as directed, there is no need of rubber caps on them during weighing.

The gas holder shown in Fig. 6 was designed by Professor Lord some years ago; it has the advantage of keeping the gas at constant pressure, a point of some importance in combustion work as variations in pressure affect the rate of flow through the furnace.

A is a drum of tinned copper 14 in. in diameter and 24 in. high. It is provided with a stop-cock, H, for drawing out the gas and a

gage, B, for showing the level of the water in the drum. I is an opening near the bottom of the drum for letting out the water when filling the tank with gas. When using the tank this opening is closed with a good rubber stopper. The gas is run into the tank through the cock H or by a tube inserted into I and small enough to allow the water to escape around it. The arrangement for forcing the gas out of the tank is as follows: Water is kept running into the cup, E, on top of the drum at such a rate as to overflow continuously through one of the side openings, F, into a sink. The head of water on the gas is determined by the opening selected, the others being closed by corks. From the bottom of this cup a pipe, D, runs down into the drum and into an interior cup, C, which fills with water and overflows through the pipe G into the bottom of the tank.

It will be seen that the water will in this way fill the tank and force out the gas and yet the "head" on the gas will always be the difference in the level between the water in the cup, E, and that in the cup, C, inside the tank and thus remain constant. The interior cup can be made smaller than shown in the figure; it is only necessary that it have volume enough to allow for the expansion and contraction of the gas due to the ordinary changes of temperature.

The oxygen may be passed into the train directly from a high pressure oxygen cylinder but the writer prefers to use the above.

Process of Analysis.—After the furnace is heated up to 1000°C., the aspirator is opened while the tube at the extreme left is closed. If the apparatus is tight no bubbles will pass through the KOH bulb after a few minutes. If it is not tight, it of course must be made so. Now aspirate oxygen or air through at the rate of four or five bubbles per second for several minutes, detach the weighing apparatus and weigh. Again attach the weighing apparatus, aspirate through 1000 c.c. of oxygen, detach and again weigh. There should not be either gain or loss in weight. If there is none, everything is ready for the determination.

Weigh 2 grams of the proper sized sample. Pour into a boat, preferably one of alundum or silica, pure alundum sand enough to cover the bottom of the boat and heap up against the sides when a trough is made in the sand with a spatula. The sand should be fine enough to pass through a 30-mesh sieve. Scatter the

sample drillings in this trough so that they do not heap up above the top of the boat, and do not touch the boat. Open the furnace tube at the left end, quickly push the boat to the middle of the furnace, and close the tube. Start the aspirator and connect to the oxygen supply. As soon as the oxygen gets to the sample combustion commences rapidly, and the oxygen will flow in with a rush, causing such rapid combustion of the iron that it will fuse unless the flow of oxygen is regulated. It should be so regulated that 2 grams of iron burn completely in three to four minutes. The end of the combustion is shown when the oxygen ceases to flow rapidly. If the combustion has been complete, about 650 c.c. of oxygen will have been used. During the combustion period, very little oxygen will be flowing through the potash bulbs, but a small amount should do so. After the combustion period, continue to pass oxygen or air through for 15 minutes. Detach the weighing apparatus and weigh. The weighing must be done promptly when the ends are not capped. If the apparatus is weighed filled with oxygen it should be capped, if filled with air the caps are not necessary. The increase in weight multiplied by $\frac{3}{11}$ gives the amount of carbon present.

In order to save oxygen, air may be aspirated through before and after the combustion, but this takes more time. The bulbs may be filled with air by detaching them from the furnace and drawing through them air dried by first passing over calcium chloride. If the bulbs are weighed with oxygen in them before the combustion they must also be weighed with the same gas after the combustion. They should be counterpoised on the balance with another set.

The weighing apparatus is again attached, the boat and its contents removed from the furnace, and all is ready for the next determination. The potash bulbs can be used 20 to 40 times before they need to be refilled.

In the case of pig-iron and many alloys, the process is just the same as above given, except that an equal weight of red lead is mixed with the drillings.

Notes on the Process.—The ends of the combustion tube should be kept cool by being wrapped with asbestos cloth, the ends of which dip in a beaker of water. It is also well to have a plug of asbestos in front

of the stoppers to protect them from heat radiation from the walls of the tube.

Steel drillings and red lead should not be spilled in the tube as they combine with the silica and destroy the tube. It is well to have a little silica sand scattered about the bottom of the tube to combine with spilled material.

The sand and red lead used should be thoroughly ignited before use in order to remove any carbon. The same is true of the boat.

The boats used may be molded of clay or may be made of silica, porcelain, alundum or platinum. The writer prefers the alundum or silica boats. Each one should last for many determinations when properly protected with sand. Boats made of molded asbestos are sometimes used.

While, as a rule, it is not necessary to use CuO in the furnace it is safest to do so in order to burn any CO which may have been formed. It may be used without injuring the silica tube as follows: A roll of CuO gauze is wrapped with asbestos paper and then placed in the tube on pieces of broken alundum boats. The CuO should be well within the furnace. A plug of palladiumized asbestos completes the precautions for complete combustion of any CO possibly present, and also protects the stopper on the exit side of the furnace from heat radiation. The palladiumized asbestos is made as directed on page 285.

The temperature of the furnace should be not less than 950° and preferably as high as 1050°C. At lower temperatures combustion of the sample is not complete.

Instead of a silica tube, a porcelain one may be used. Porcelain breaks more easily than the silica tube when heated or cooled. Platinum tubes are used in some works and are very desirable but their first cost is very high.

It must be remembered that the CO and CO_2 dissolved in steel will be included in the carbon obtained by this method. This may make the results as much as 0.05 per cent. too high.

If a large soda-lime tube or bottle is used to absorb the CO_2, and P_2O_5 for drying the gas, the oxygen may be passed through as fast as 400 c.c. per minute and the combustion and absorption may be done in six minutes. Special precaution is necessary to protect the tube from spattered oxide of iron. (Fleming, Chem. Eng., XVII, 80.)

Barium Carbonate Method for Carbon

On damp days it is difficult to weigh a large absorption apparatus accurately on account of the varying amounts of moisture on the surface

of the glass at different weighings. Consequently many chemists prefer to absorb the carbon dioxide in barium hydroxide solution and weigh or titrate the $BaCO_3$. This is carried out as follows:

Process of Analysis.—In place of the weighing apparatus (potash bulbs or soda-lime tube) attach a Meyer tube (M, Fig. 6a) in which has been put 100 c.c. of a saturated $Ba(OH)_2$ solution. Carry on the combustion as directed above and when the CO_2 has all been absorbed filter off the $BaCO_3$ according to the following directions. Connect the absorption bulb as shown in Fig. 6a. S is a two-way stop-cock connected with suction. The bubble tube (Meyer tube) is fitted with two rubber stoppers through which short pieces of glass tubing pass. The filter C contains an ashless filter paper. Insert the stopper in the funnel and connect it with the Meyer tube as shown in the drawing and apply very gentle suction. When necessary open P_3 to admit air back of the liquid after the contents of the tube have all been transferred to the filter bottle, half fill the large bulb nearest B with water by opening the pinch-cock P_1; operate the stop-cock S during this and subsequent operations so as to maintain gentle suction. Manipulate the tube M so as to bring the wash water into contact with all parts of the interior and then suck out the water through C; during this and the subsequent washings leave the pinch-cock P_2 open. After eight washings, allowing the wash water to drain off thoroughly each time, detach M and complete the washing by filling C to the top with water free from carbonic acid, sucking dry and repeating the operation once more.

Burn off the filter paper at a *dull red* heat and weigh the $BaCO_3$. The weight multiplied by 0.0608 gives the carbon.

To determine the carbon by titration proceed as follows: Put the filter paper and contents in a small flask, add an excess of N/10 HCl, and shake the flask to open the paper, add a few drops of methyl orange solution and titrate the excess of acid with N/10 NaOH. The difference between the amounts of N/10 acid and alkali used multiplied by 0.0006 gram gives the carbon.

See page 57 for direction for preparation of N/10 HCl and N/10 NaOH.

Notes.—One hundred and fifty cubic centimeters wash water will dissolve about 0.0003 gram $BaCO_3$ = 0.000018 gram carbon. This

would be negligible for present purposes, and the amount dissolved would be really less than this because of the repression of solubility during the first washings by the barium hydroxide still present; also it is quite possible that in the rapid passage through the filter there has not been sufficient time for the wash water to become saturated with barium carbonate.

When using this method the calcium chloride in the purifying and absorbing trains is not necessary.

When working with steels high in carbon (above 1 per cent.) it is advisable not to use more than 1 gram, in order that filtration may be sufficiently rapid. For very accurate work the Meyer tubes should be washed with dilute acid before beginning work each day. After a de-

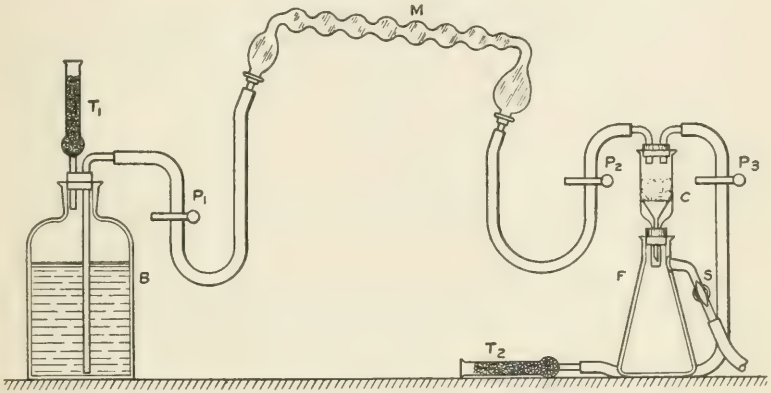

FIG. 6a.

termination is finished, the Meyer tube should be completely filled two or three times with tap water, then rinsed with distilled water, in order to remove the carbon dioxide liberated when dissolving the carbonate from the previous determination.

The flask containing the carbonate should be very thoroughly agitated after adding the acid, since the carbonate sometimes dissolves rather slowly if this is not done; this is particularly the case if it has packed much during filtration.

The rubber tube connecting B (see Fig. 6a) to the Meyer tube should be washed with a little water from B, before beginning determinations each day.

REFERENCE:

CAIN, *J. Ind. Eng. Chem.*, 6, 465 (1914).

Other Direct Combustion Processes.—For alloys, F. Wüst mixes the sample with five times its weight of a powdered alloy composed of three parts of tin and one part of antimony and ignites in a current of oxygen at 900°C. Combustion is complete in 10 minutes. (Metallurgie, VII, page 321.)

DeNolly and Queneau burn the sample of steel in a flask. The sample is suspended in a boat in the flask and is ignited by means of electricity applied by means of a pair of electrodes which touch the drillings. A current of oxygen is directed on the drillings until combustion is complete. The CO_2 is absorbed in a known volume of standard alkali which is titrated after the flask is cool. Sulfur is said not to interfere. Time required is 5 to 7 minutes. (See DeNolly, Chimiste, III, 26; Queneau, Met. Chem. Eng., IX, 441.)

Mahler and Goutal employ a bomb and burn the sample in oxygen at eight atmospheres pressure. The drillings are fired electrically by means of a fine wire as in calorimetry. The gas is passed through $Ba(OH)_2$ which is titrated with oxalic acid. (Compt. rend., CLIII, 549.)

The Determination of Carbon in Pig-iron and Steel Involving Separation of the Carbon from Iron

When a sample of iron is dissolved in a strong solution of K_2CuCl_4 all of the carbon in the sample is left undissolved, whether it be present as graphite, combined as Fe_3C or in solid solution as austenite. The reactions may be represented as follows:

$$Fe+K_2CuCl_4=FeCl_2+Cu+2KCl$$

and

$$Fe_3C+3K_2CuCl_4=3FeCl_2+3Cu+C+6KCl$$

The copper then redissolves as follows:

$$K_2CuCl_4+Cu=2KCuCl_2$$

The carbon liberated can be filtered off and ignited to CO_2 by either wet or dry oxidation.

It is essential that there be no hydrogen liberated during the solution of the iron or hydrocarbons will be liberated causing loss of carbon. The method cannot be used on some alloy steels or ferro-alloys because of such loss of carbon. According to Moore and Bain (J. Soc. Chem. Ind., XXVII, 845) when steel is dissolved in K_2CuCl_4, there is a slight loss of carbon or hydrocarbon. The higher the percentage of carbon in solid solution, the greater seems to be the loss. Thus the loss is

greater on a hardened steel than on the same steel after annealing. (DILNER, J. Iron and Steel Inst., Vol. XI, 1904, p. 255.)

The carbonaceous residue often contains some silica and phosphide of iron and sulfide of copper. Alloy steels may also give a residue of tungsten, chromium, vanadium and molybdenum.

The KCl serves to hold the cuprous salt in solution and greatly hastens the action.

This solution has a tendency to dissolve organic matter, which is liable to be subsequently precipitated with the carbon in the steel. This is especially true of the ammonium salt, it being very difficult to obtain it free from organic matter (derived from the ammonium salts used in its manufacture). The salt should be thoroughly purified by recrystallization. The potassium salt is more easily obtained free from this contamination and for this reason is to be preferred.

A large excess of the solution is required to prevent separation of metallic copper with the carbon.

The carbon residue retains chlorides very difficult to wash out, which cause trouble in the subsequent combustion. If any metallic copper is precipitated and left mixed with the carbon, it will form basic subchlorides nearly insoluble in water. The spongy carbon is best freed from chlorides by treating with dilute HCl and then washing thoroughly with water.

Instead of using a neutral solution of potassium cupric chloride, it is usually acidified with a little HCl. The presence of this acid will cause no loss of carbon, provided the solution is kept cool while the iron is dissolving.

The solution after having been used can be regenerated and used again by passing chlorine gas through it until the Cu_2Cl_2 is changed back again to $CuCl_2$.

REFERENCES:

SARGENT, *J. Am. Chem. Soc.*, 1900, p. 210.

For important papers on the carbon determination consult—

Trans. Am. Inst. Mining Eng., XIX, p. 614.

J. Anal. and App. Chem., V, p. 129.

J. Anal. and App. Chem., V, p. 122.

J. Am. Chem. Soc., 1893, p. 448, 526; 1895, p. 873; 1898, p. 243.

Process. Solution of the Metal and Separation of the Carbon.—Prepare a solution of the double chloride of copper and ammonium or potassium. Use the purest crystallized salt obtainable. Dissolve one part in three parts of pure water, free from grease or organic matter, adding about 5 per cent. of concentrated

HCl. Let the liquid settle, decant off the *clear* solution, and filter any turbid portion through ignited asbestos.

Weigh out 2 grams of pig-iron, 3 grams of high-carbon steel or 5 grams of low-carbon steel or wrought iron. Put this metal into a 200 or 250 c.c. beaker, and add at once the copper solution, using 50 c.c. for each gram of the sample taken. Stir the liquid continuously until the iron is dissolved.

If an air blast is available, this stirring can be accomplished by blowing air through the liquid. The air should be first passed through a tube filled with absorbent cotton to filter out any dust.

The completion of the reaction is recognized by the residue becoming light and "flotant." At first more or less copper will separate, but continued stirring will bring it into solution.

As soon as all the separated copper has disappeared, let settle a few minutes if necessary and decant onto an asbestos filter, disturbing the carbon as little as possible. Add 10 c.c. of dilute HCl (1 : 1), washing down the sides of the beaker with this acid. Decant this through the filter. When the liquid has all run through wash out the beaker and transfer all adhering carbon to the filter with the dilute HCl.

Wash the carbon on the filter twice with acid. Let the acid run through slowly to give it time to act. Now wash with water until all the HCl is removed and the filtrate does not react with $AgNO_3$.

The filtrate will be dark colored at first, but when diluted with the HCl and water will become lighter, and then must be carefully examined to see that no particles of carbon have run through the filter.

The drillings of metal must be free from all *grease* or intermixed particles of wood, straw or paper. They may be separated from the latter by a magnet, and from the former by washing them with pure ether, and drying. Care in drilling and handling the sample will render this treatment unnecessary.

The weighing out of pig-iron for this carbon determination is a matter of great difficulty, as the fine, dusty portion is usually higher in carbon than the lumps. A method proposed by Dr. Shimer is to moisten the drillings with alcohol, so that the fine may stick to the coarse. Then take a portion of approximately

the right weight, put it on a weighed watch-glass, dry it carefully and reweigh. Use this amount in the determination.

Preparation of the Asbestos Filter.—The form of filter shown in Fig. 7 is a slight modification of one described by Professor Arnold in his "Steel Works Analysis." It will be found very convenient. A is an ordinary heavy glass filtering flask such as is used with the Bunsen filter pump. It should have a capacity of about 500 c.c. B is a piece of glass-tube with a uniform bore of about $\frac{5}{8}$ in. and about 9 in. long. This passes through the rubber stopper in the neck of the flask. The hole in this stopper can be drilled with a large cork borer moistened with a dilute solution of KOH. Into this tube a second tube C is inserted. This is of such a size as to just slip freely through the larger tube. It should be about 1 in. longer than the first tube and have the ends ground off square. The apparatus should be so arranged that when the smaller tube rests on the bottom of the flask it will leave about two-thirds of the upper tube unoccupied. Now cut a disc of platinum foil of such a size that it will freely slip into the larger tube and rest in place on the end of the inner tube. This platinum disc should be punched full of holes with a needle. It is advantageous to solder (with a bit of gold and a blow pipe), a piece of stiff platinum wire, E, to the center of this disc which will stick down into the lower tube and keep the disc in place. This wire will also serve as a convenient handle for lifting the platinum from the asbestos mat after it is removed from the tube.

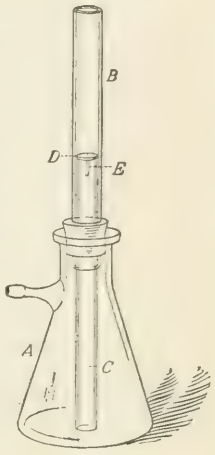

FIG. 7.

Prepare the asbestos for the felt as follows: Select long-fibered asbestos. (Not the "cottony" kind, but that with rather stiff fibers.) Cut it across the fiber into pieces $\frac{3}{16}$ in. long. Ignite these in a platinum crucible at a low red heat for at least 30 minutes. When cool transfer them to a clean porcelain mortar and "macerate" them to a pulp with strong HCl. Now dilute the paste with a large amount of water, pour into a beaker and allow the mixture to settle until the fibrous mass collects at the

bottom, leaving the fine, milky silt still in suspension. Decant from the fibers and repeat the washing until the wash water comes off only slightly milky. Asbestos prepared in this manner makes a felt that filters very rapidly. If the fine slimy material that is formed during the felting is left in the mixture it will clog the filter and make it work badly. Preserve the felt in water in a stoppered bottle. To form the filter pour enough of the suspended felt into the tube to form a layer about $\frac{1}{16}$ in. thick when drawn down by suction onto the platinum disc in the tube, then attach the suction pump. Exactly the right amount must be learned by experience. But when right it will filter rapidly and yet retain the finest carbon.

Draw a little water through the felt to wash it before pouring on the carbon solution. After the carbon is filtered and washed take the stopper with the tubes out of the bottle, wash off the smaller tube and then push it carefully through the larger tube, forcing out from below the disc carrying the felt and carbon. The felt and carbon can now be dropped into the combustion flask or into a platinum boat for combustion in oxygen. With a little care no carbon whatever will be left adhering to the tube. Should a little adhere it can be washed off into the flask with a few drops of water or wiped off with a small tuft of ignited asbestos.

The boat containing the carbon is now analyzed for carbon in the furnace as previously described for the direct combustion of carbon in steel. The mass should be dry before putting it in the furnace.

If a furnace is not available, the following wet oxidation method will give good results.

Determination of the Carbon by Oxidation with Chromic Acid

Carbon in any form is rapidly and completely oxidized to CO_2 when heated with chromic acid and an excess of sulfuric acid.

It is essential that the sulfuric acid be sufficiently concentrated; if too dilute, the oxidation will be incomplete and some CO will be formed which will escape the absorption apparatus. The strength of acid necessary depends somewhat on the condition of the carbon, as the amorphous carbon from steels is more easily oxidized than the graphite from pig-iron. In no case should the mixture contain less than 70 per cent. of

H_2SO_4, while for pig-irons enough should be present to give, on boiling, a trace of white fumes of H_2SO_4. If not present in large amount these white fumes will be arrested in the purifying train. They represent only a very minute quantity by weight. When the acid is of this strength the mixture will give off some oxygen gas on boiling.

If the carbon retains chlorine or chlorides, chlorine and chloro-chromic acid gas may form, escape with the CO_2 and be absorbed by the KOH, vitiating the results unless special means be provided for absorbing them in the purifying train.

The H_2SO_4 used must be purified from all organic matter.

Arrangement of the Apparatus.—Fig. 8 shows a convenient form of train for the use of students. It is compact, needs no special clamps, and can be taken apart and set away in a laboratory desk. C is an Erlenmeyer flask of about 250 c.c. capacity, fitted with a two-hole rubber stopper; into one hole is inserted a bulb funnel tube B, having a glass stop-cock, and into the other a delivery tube M for the gas.

This latter should be of rather large diameter and so inclined that everything condensing in it will run back into the flask. It is a good plan to have it cooled by a "water jacket" D, consisting of a larger tube surrounding the smaller, the space between the two being filled with water.

A small guard tube A, filled with "soda lime" is fitted to the top of the funnel tube.

This serves to remove any CO_2 from the air drawn into the flask. It must be so arranged as to be easily connected and disconnected.

The delivery tube is connected with the purifying and absorbing apparatus (or "train") arranged in the order shown.

E is a bottle of 50 or 75 c.c. capacity, containing about 30 c.c. of a solution of silver arsenite in dilute sulfuric acid.

This serves to absorb any chlorine, HCl or CrO_2Cl_2 in the gas. A solution of silver sulfate may be used instead, but this does not absorb chlorine nor chromyl chloride and is usually preceded by a bottle containing pyrogallic acid dissolved in a solution of potassium oxalate (Langley). When using the arsenite this is unnecessary, as it is oxidized to arsenate by the chlorine and the silver precipitated as chloride.

The arsenite solution is prepared as follows: Dissolve 2 grams

of pulverized As_2O_3 in the smallest possible quantity of a dilute solution of KOH. Dilute to 250 c.c. and add dilute H_2SO_4 till the solution is neutral to litmus paper. Now add a solution of $AgNO_3$ as long as a yellow precipitate forms, carefully keeping the solution neutral by adding a solution of KOH drop by drop as needed. Stir the liquid till the precipitate clots, let it settle, and wash it thoroughly by decantation. Finally dissolve the precipitate in a slight excess of dilute H_2SO_4 (10 per cent.).

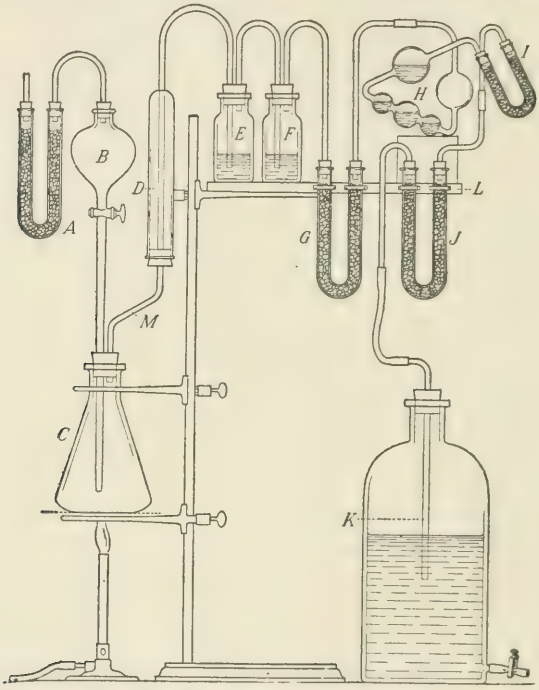

FIG. 8.

Dilute to about 150 c.c. and filter from any undissolved AgCl. The solution keeps well.

The silver sulfate is made by dissolving about 0.5 gram of $AgNO_3$ in a little water, adding 1 c.c. concentrated H_2SO_4, evaporating till the HNO_3 is all expelled, cooling and diluting largely with water. Ag_2SO_4 is only sparingly soluble.

F is a bottle containing 20 or 30 c.c. of pure concentrated H_2SO_4.

This takes out all the water vapor from the gas.

G is a U-tube containing granular $CaCl_2$. Fill about an inch of the tube, on the side next to the H_2SO_4 with cotton and moisten the top of this with a drop of water (Blair). It is shown with its connecting tube in Fig. 9, C.

The object of this $CaCl_2$ is to absorb water and to bring the gas stream entering the absorption apparatus (H and I) into the same condition as to moisture, in which it leaves it. H_2SO_4 will dry air more completely than $CaCl_2$, hence if the gas entered through H_2SO_4 and left through $CaCl_2$ it would carry out more moisture from the KOH bulbs than it brought in and so result in loss of weight. It also serves to catch any white fumes of H_2SO_4 carried over by the gas.

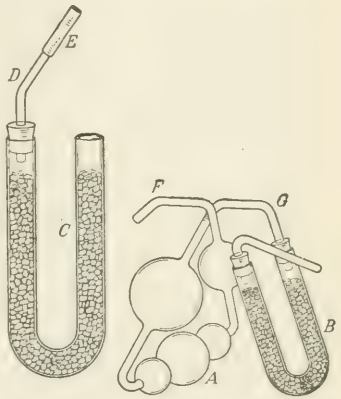

Fig. 9.

Dried $CaCl_2$ and not the fused salt should be used. This latter is usually alkaline from free CaO and will absorb some CO_2.

H (Fig. 9) shows the Liebig's potash bulbs. These contain a clear solution of KOH of about sp. gr. 1.27 (about 30 per cent.). This solution absorbs the CO_2 but not *completely* unless the gas stream is slow. The solution gives up a little water to the gas passing through. If made stronger than directed it deposits K_2CO_3 which may clog up the tube.

As caustic potash frequently contains nitrites and almost invariably traces of $Fe(OH)_2$, a fresh solution will absorb oxygen, the $Fe(OH)_2$ gradually precipitating as $Fe(OH)_3$. If the potash bulbs are filled with such a solution they will frequently continue to increase in weight for some time if air alone is aspirated through them. This troublesome difficulty may be entirely overcome if the potash solution is heated to boiling before using and a solution of potassium permanganate added drop by drop until a faint persistent green tint is produced. The liquid is then allowed to cool and settle, and the clear solution decanted for use.

I is a small U-tube, with the limb next the potash bulbs filled

with granular soda lime. This should not be too dry. The other limb is filled with granular $CaCl_2$.

This tube serves to catch the trace of CO_2 escaping the bulbs, and also to retain the moisture carried over from the potash bulbs. Soda lime is a more rapid and complete absorbent for CO_2 than the KOH in the bulbs, but it is soon exhausted. By letting the bulbs do most of the work and only using the soda lime as a guard, it lasts for many operations and retains every trace of the CO_2. The potash bulbs and the soda lime—calcium chloride—tube are the parts of the train to be *weighed*. They may be weighed separately or together. In the latter case they should be permanently combined into one piece as shown in Fig. 9, A and B, a very convenient arrangement. The ends of the tubes are bent over, as shown at F and G (Fig. 9). When connected up, the tube and bulbs should so support each other as to stand upright safely.

J is a U-tube similar to the last, but larger, having the limb next to I filled with $CaCl_2$, and the other with granular soda lime.

This serves as a guard tube to prevent moisture or CO_2 working back into the absorption apparatus from the aspirator. It can be used almost indefinitely without becoming exhausted.

K is an aspirator for sucking air slowly through the apparatus.

This must be arranged so that it can be easily attached and detached. It can be made from a 5 pint acid bottle by boring a hole near the bottom with a pointed file dipped in turpentine, fitting a glass tube in this by a rubber ring and then attaching to this a rubber tube and pinch-cock.

Notes on the above Apparatus.—It is essential that none of the chromic acid solution come into contact with the rubber stopper or connections, as it would, of course, form CO_2. For similar reasons it is necessary that the glass stop-cock in the funnel tube be free from grease of any sort.

A flask provided with a ground glass cap, into which the tubes are fused, may be substituted for the rubber stoppered flask as described.

Liquids always absorb some CO_2, hence the volume of all absorbing liquids used in the purifying train must be small. The CO_2 absorbed is, however, given up again to a current of air passed through them for some time.

Setting up and Testing the Apparatus.—The connection tubes are united by short rubber tubes. These must be carefully tied with thread or wire or rubber band, as it is essential that the whole apparatus be air tight. Rubber stoppers are, of course, the best, but good ordinary corks can be used if rolled soft and carefully bored and fitted. Sealing wax should not be used on these corks to make the joints tight, as it is liable to crack and leak unexpectedly. The potash bulbs and U-tube may be "capped" when disconnected, by short rubber tubes closed with bits of glass rod. These caps must always be removed for a moment and then replaced just before weighing, that the air pressure inside and outside the bulb may become equal.

If the ends of the glass tubes are heated until they draw together leaving only a small opening the size of a knitting needle, the rubber "caps" need not be used, provided the weighing is promptly done, as these small holes will not admit of any noticeable diffusion of moisture into the bulbs.

It is desirable to pass some CO_2 through the apparatus after first setting it up, in order to saturate any alkaline material present in the $CaCl_2$, etc. When this is done the weighed part of the train is, of course, omitted. Connect up the train, leaving out the parts H, I and J. Put a little marble in the flask, and add a little dilute H_2SO_4 to generate a slow stream of CO_2. Let this run through the portion of the train remaining for about 30 minutes. Disconnect and wash out the flask, replace it, and then aspirate air until 3 or 4 liters have been slowly drawn through the apparatus.

Now connect up the whole train and attach the aspirator. Close the stop-cock in the funnel tube of the flask and see if all connections are *tight*. This is shown if the water entirely stops running from the aspirator. Let in air cautiously by opening the stop-cock in the funnel tube. Attach the soda lime guard-tube to the funnel tube and aspirate 1 or 2 liters of air carefully (not over four or five bubbles a second). Disconnect the bulbs and the U-tube, cap them, and wipe them carefully. Set them in or near the balance case until they attain its temperature (10 or 20 minutes). Uncap them a moment, replace the caps and then carefully weigh them. Replace them in the train and aspirate 1500 c.c. more of air, detach and reweigh them. The KOH

bulb will lose (due to giving up moisture) and the U-tube will gain weight. The loss in one must equal the gain in the other. The total weight of the absorption apparatus must not change more than ½ mg.

Treatment of the Carbon Residue from the Iron.—Transfer this to the flask C, using as little water as is necessary to wash out the filter tube. The total amount of liquid in the flask must not exceed 20 c.c. Now dissolve 4 grams of chromic acid in 4 c.c. of water, and pour it into the flask through the funnel tube, following it with 2 or 3 c.c. of water to wash out the tube. Now put into the bulb of the funnel a quantity of concentrated H_2SO_4, equal to about two and a half or three times the volume of the liquid in the flask.

This volume can be estimated by pouring water into a second similar flask until it appears to contain the same amount of liquid as the first and then measuring the quantity used.

The acid used should be purified from any trace of organic matter that it may contain, by adding a little chromic acid to a quantity of it and then heating it to about 200°C. for a few minutes. Let it stand till cool before using.

Now open the stop-cock and run the acid slowly into the flask, being careful to avoid too violent action. When the acid is all in, shake the flask carefully to mix the contents.

The evolution of CO_2 will begin at once. Finally heat carefully to boiling, so regulating the heat that the evolution of the gas does not take place too rapidly. The gas should not pass through the potash bulbs faster than two or three bubbles per second. The boiling should be continued for two or three minutes. At the end of this time but little gas should be coming over through the bottles; but as some oxygen is likely to be given off by the chromic acid mixture, it is usually not possible to continue boiling till the evolution of gas ceases. Now withdraw the lamp and immediately open the stop-cock of the funnel tube to admit air and prevent back suction. Connect the funnel tube with the soda-lime guard tube, and let the apparatus cool a few minutes. Then aspirate carefully until a volume of air has been drawn through equal to seven or eight times the capacity of the apparatus.

Detach the absorption apparatus and weigh it. The total

gain in weight will be the amount of CO_2 formed, and this multiplied by 0.2727 gives the amount of carbon in the sample taken.

The greatest care and "handiness" are necessary, but with skill duplicates should agree within 0.01 per cent.

The solution should not be brought to the boiling-point too rapidly. By raising the temperature slowly time is given for the reaction and most of the carbon will be oxidized before the liquid begins to boil. If much unoxidized carbon is present in the boiling liquid, particles of it are likely to be carried up onto the sides of the flask where they will adhere and so escape oxidation.

If white fumes form toward the end of the boiling, let the flask cool until they disappear before aspirating.

The foregoing method of determining carbon by combustion with chromic acid is very accurate if conducted carefully. It has the advantage of demanding no special or expensive apparatus.

The Determination of Carbon in Steel by Color

This method is in general use in steel works. It depends upon the fact that when steel is dissolved in dilute HNO_3 a brown compound containing the carbon forms. This goes into solution, on boiling, coloring the liquid more deeply as the percentage of carbon is higher. Pure iron dissolves in HNO_3, sp. gr. 1.2, giving a nearly colorless solution, and from which every trace of color is removed by moderate dilution.

The color produced by the carbonaceous matter is rapidly altered by light. Its depth depends somewhat on the mode of solution, the concentration of the acid and the kind of steel, hence the process must be conducted strictly according to rule to get concordant results.

There is required: First, a standard steel, which must be of exactly the same kind as that to be tested, and also similar in its composition and of approximately the same carbon percentage. The carbon in this must have been accurately determined gravimetrically. Second, nitric acid of sp. gr. 1.2, perfectly free from chlorine, the least trace of which will seriously alter the color of the iron solution, making it more yellow. The above strength corresponds to one volume of concentrated acid to one volume of water. Third, comparison tubes of clear white glass, graduated in $\frac{1}{10}$ c.c., and of exactly equal diameters.

For comparing the colors an arrangement such as is shown in Fig. 10 is convenient. It consists of a wooden box open at one end and closed by a sheet of ground glass at the other. The glass is covered with black

paper, except the two slits, A, before which the tubes are placed and compared by the observer, who looks into the large end of the box. The tubes are carried by a little rack, B, which can be revolved by turning the knob, C, and the tubes thus reversed without taking them out of the box. This reversal of the tubes is important, as the eye will usually see the right-hand tube darker. In the absence of such a "camera" a piece of wet paper on a window makes a good temporary background. Many kinds of colorimeters are on the market.

If the steel contains much sulfur the solution will be slightly *turbid* from free S. Comparison is difficult in this case.

The volume of acid used should bear some relation to the percentage of carbon present. The amount of metal taken must be increased when the carbon is low. It is essential that both standard and sample be treated exactly alike, as to the amount of sample taken, time of heating and volume of acid. It is especially important that the standard and the sample should have undergone the same "heat treatment" in their manufacture. Only the combined carbon is determined by the color method, any free carbon present not affecting the color.

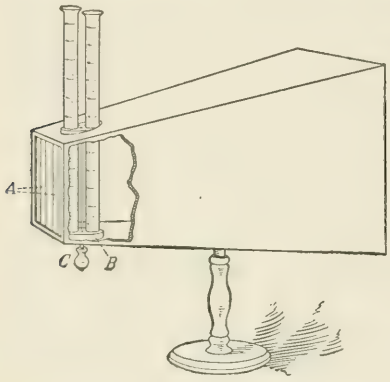

FIG. 10.

Process of Analysis.—Weigh 0.2 gram of the steel and of the standard, each into a 6 in. test tube. Add to each tube a measured volume of cold HNO_3 sp. gr. 1.2, using the following amount: For steels with not over $\frac{2}{10}$ per cent. carbon, 4 c.c.; from $\frac{2}{10}$ to $\frac{5}{10}$ per cent. 6 c.c.; from $\frac{5}{10}$ to 1 per cent., 8 c.c.; and over 1 per cent., 10 c.c.

Stand the tubes in cold water till violent action ceases. Then set them in boiling water and heat until the solution is perfectly clear and no more fine bubbles of gas appear. Keep the mouths of the test-tubes closed loosely by little glass bulbs or balls to prevent drying of the iron salts on the sides of the tubes. The time required will be from 15 to 30 minutes, according to the percentage of carbon in the steel. Now cool the tubes in water. Add an equal volume of water to each and pour into the comparison tubes. Dilute carefully until the colors match. The

percentages of the carbon will be to each other as the volumes of the liquids in the tubes.

Where a number of steels are to be tested at once it is convenient to dilute the standard until each cubic centimeter represents some definite percentage of carbon, and then match it with the others, so that the readings in cubic centimeters can be readily converted to per cents. For example, if the standard contained 0.38 per cent. C, dilute it to 19 c.c., then if a comparison showed the unknown steel to read 16 c.c. it would obviously contain 0.32 per cent. carbon.

Where the color carbon process is used on steels of comparatively uniform contents, it is usual to take 10 c.c. of acid and then enough of the sample to give a sufficiently marked color with this amount; for example, 0.5 gram of steel and 10 c.c. of acid. In the case of very low carbon steel (under 0.2 per cent.) 1 gram of steel may be dissolved in 20 c.c. of acid.

Notes on the Process.—The color process can be applied to pig-iron and gives an approximate determination of its combined carbon. In this case a solution of the sample and of the standard must each be filtered through a small filter and the solutions compared. Filters of the same size and a pig-iron standard must be used.

The use of permanent standard colors, either organic or inorganic, such as the mixed chlorides of iron, copper and cobalt, has been tried. This is not advisable as it does not provide for the variations in color due to slight differences in the treatment, as well as does the treatment of standard and sample together. For these methods see Trans. Am. Inst. Mining Eng., I, p. 240, and XVI, p. 111.

For very low carbon steels the color is faint and uncertain. An alkaline method has been used on such metals. (See Stead, J. Iron and Steel Inst., 1883, No. 1, p. 213.)

The Determination of the Graphite in Pig-iron

When pig-iron is boiled with HCl or dilute HNO_3 the combined carbon is converted into solid, liquid, or gaseous hydrocarbons or nitro compounds; while the graphite is all left insoluble. The non-volatile hydrocarbons are soluble either in alkalies, in alcohol, or in ether. The graphite or uncombined carbon is not acted upon by any of these reagents but remains in the residue as a black mass. The residue may also contain hydrated silica and frequently titanium carbide and free sulfur.

The silica holds water tenaciously and cannot be thoroughly dehydrated below a red heat. Titanium carbide is decomposed by HNO_3 but not by HCl; while sulfur is separated by dilute HNO_3 but not by HCl. Graphite is not at all oxidized by HNO_3, sp. gr. 1.2. The use of nitric acid is preferable with gray irons low in combined carbon, while HCl is better for white iron high in combined carbon and for ferrosilicons as these only dissolve with difficulty in HNO_3. The carbon in the residue can only be accurately determined by combustion.

References:

Shimer, *J. Am. Chem. Soc.*, Vol. XVII, p. 873.

Drown, *Trans.* Am. Inst. Mining Eng., Vol. III, p. 41.

Process of Analysis.—Treat 2 grams of drillings in a beaker with 50 c.c. of HCl, sp. gr. 1.12. Cover and boil briskly for 30 minutes. Dilute, filter on an asbestos filter and wash with hot water until all iron salts are removed. Then pour on a little HCl and wash again with water. Now wash the residue with a 30 per cent. solution of caustic soda, then with water, then with alcohol, then with ether, and finally with cold water, then hot water till every trace of ether is extracted. Now transfer to the carbon apparatus and determine the carbon with chromic acid and sulfuric acid, or by combustion in oxygen.

This complicated washing is required to remove the solid and liquid hydrocarbons which are likely to form and are insoluble in water alone. The ether must be followed by cold water; if hot water were added at once, it would make the ether boil and might throw the carbon out of the filter tube. Nitric acid of sp. gr. 1.135 can be substituted for HCl with such irons as are readily dissolved by it. If a little HF is added to the solution after the metal is dissolved it will frequently greatly facilitate the filtration by preventing the separation of silica in a gelatinous form. By using a sufficient quantity of acid of the right specific gravity, most of the silica will usually remain in solution.

Determination of the Graphite by Direct Weighing

This method gives satisfactory results on many irons. It is quite generally used as a rapid method. It should be checked by the combustion method when applied to kinds of iron not previously tested.

The residue is dried at 100°C. and then burned and the loss of weight assumed to be carbon. Any sulphur or water that the residue contains will, of course, be rated as carbon.

Process.—Weigh out 2 grams of the drillings into a 250 c.c. beaker. Add 100 c.c. of HCl, sp. gr. 1.1, or of HNO_3, sp. gr. 1.135. Boil gently till all action ceases. Keep the beaker covered to prevent evaporation and concentration of the solution which may cause the separation of silica. Finally add three or four drops of HF and boil again. Prepare a Gooch perforated crucible as follows: First, heat, cool and weigh it; second, fit into the bottom of the crucible a disc of ashless filter paper and dry the paper and crucible at 100° for 20 minutes and weigh again. Filter the solution through this crucible in the ordinary way, transferring the residue with cold water. Then wash the residue with hot dilute HCl, then with hot water, and then with a 5 per cent. solution of NH_4OH. When the filtrate runs through colorless finally wash with a mixture of equal parts of alcohol and ether. Now dry the crucible and contents at 100°C. to constant weight which will take from 10 to 20 minutes. Now set the crucible over a Bunsen burner flame and burn off the residue. When all the carbon has burned away, weigh the crucible again.

By subtracting the weight of the crucible with the filter paper, from the weight of the crucible plus the filter paper plus the residue, the weight of the residue is obtained. Subtracting the weight of the empty crucible from the final weight of the crucible plus the incombustible portion of the residue, gives the silica and other mineral matter with the carbon. Subtracting this remainder from the total weight of the carbonaceous residue gives the weight of the graphite. A still better way is to use an asbestos mat in the Gooch crucible.

Instead of using a Gooch crucible, two small tared filters can be taken and the residue then burned out in an ordinary crucible, but this is not nearly so convenient.

The above method is essentially that given by A. B. Harrison in "Methods of Iron Analysis used around Pittsburg," 2nd edition, p. 85.

References:

For variations of the method and discussion of the results consult:

Daugherty, *Chem. News*, Sept. 8, 1899.

Crobaugh, *J. Am. Chem. Soc.*, 1894, p. 104.

Auchy, *J. Am. Chem. Soc.*, 1900, p. 47.

CHAPTER IX

THE DETERMINATION OF NICKEL AND COBALT IN STEEL

The method for nickel here given is that of Moore modified by Johnson. It is very rapid and accurate and no elements interfere except copper and cobalt which are usually present in steel in very small amounts. The copper reacts like nickel and if present in more than traces must be separated as directed on page 173.

The method depends upon the following reaction:

$$Ni(NH_3)_6SO_4 + 4KCN = K_2Ni(CN)_4 + K_2SO_4 + 6NH_3.$$

This reaction takes place in a solution slightly alkaline(with ammonia) and a very large amount of iron may be present without interfering if before making alkaline a large amount of citric acid is added. The citric acid which has the formula

$$\begin{array}{l} CH_2COOH \\ | \\ CH—C—COOH \\ | \\ CH_2COOH \end{array}$$

combines with the iron to form un-ionized iron citrate which does not allow the iron to precipitate when the ammonia is added.

The end point of the reaction between the nickel and the cyanide is shown by the disappearance of a turbidity due to the presence of silver iodide. The reaction is:

$$AgI + 2KCN = KAg(CN)_2 + KI.$$

Process of Analysis.—Dissolve 1 gram of steel drillings in a 150 c.c. beaker with 20 c.c. of 1 : 1 hydrochloric acid. When action ceases add 10 c.c. of 1 : 1 nitric acid.

Reduce the volume to 15 c.c., remove the beaker from the heat and pour into it 8 c.c. of sulfuric acid diluted with 25 c.c. of water. Transfer the contents of the beaker to a 400 c.c. beaker containing 12 grams of powdered citric acid and stir until it is all dis-

solved. Make the solution faintly but distinctly alkaline with 1:1 NH_4OH. Do not add much excess as it causes low results. Cool the solution and dilute to about 300 c.c. If it is turbid, filter it.

Add to the cold solution 2 c.c. of a 20 per cent. solution of potassium iodide and then run in from a burette a standard solution of silver nitrate with stirring until a distinct turbidity due to silver iodide is produced. Then titrate with the standard cyanide. Run in the cyanide with constant stirring until the turbidity just disappears. The cyanide first reacts with the nickel then attacks the iodide. If it is thought that the end point is passed add another measured amount of silver nitrate until a turbidity is formed and again titrate with the cyanide until the turbidity just disappears. It is best to have another beaker containing a solution to be titrated to which no silver nitrate has been added sitting beside the one being titrated so as to have a clear solution of the same color to compare with. If the citric acid was dirty, the solutions will be cloudy and should be filtered before the silver nitrate is added.

Standardization of the Solutions.—Dissolve about 5 grams of KCN and 5 grams of KOH in water and dilute to 1 liter. The KOH makes the KCN solution keep better. Also dissolve 2.925 grams of $AgNO_3$ in water and dilute to 500 c.c. One cubic centimeter of each will be equal to about 0.001 gram of nickel. To standardize them, weigh out 1 gram of nickel-free steel and add 0.3370 grams of $NiSO_4(NH_4)_2SO_46H_2O$, which contains 14.85 per cent. of nickel, and treat just as above directed for a nickel steel up to the point of titration. Make the titration carefully until the turbidity just disappears. Now add 10 c.c. of the cyanide in excess and titrate with the silver nitrate until a turbidity just appears. This second titration gives the relation between the silver nitrate solution and the cyanide solution. For example, suppose that in the first place 0.5 c.c. of silver solution were added and 50.5 c.c. of cyanide were used. Then suppose that it took 10.8 c.c. of silver nitrate solution to produce a turbidity after the 10 c.c. of extra cyanide was added. The cyanide required to titrate the nickel would be $50.5 - 0.5 \times \frac{10}{10.8} = 50.04$ c.c. Since the amount of nickel present was 0.3370×0.1485 or 0.050

gram, the strength of the cyanide is $0.050 \div 50.04 = 0.0009992$ gram Ni per cubic centimeter.

Notes on the Process.—The presence of sulfates is necessary to obtain a sharp end reaction. Silver iodide is soluble in a large excess of NH_4OH, so care should be taken to have the solution only slightly alkaline with NH_4OH. But it must be alkaline.

If the titrated solutions are allowed to remain in the open beakers for some time a white film forms on the surface but no account is to be taken of it.

When chromium is present, proceed exactly as described above except to add 24 grams of citric acid. Instead of using so much citric acid some chemists use citric acid and sodium pyrophosphate.

The silver nitrate solution used should not be stronger than that indicated above, for when a strong silver solution is used, the silver iodide instead of forming a turbid solution settles out as a curdy precipitate which does not readily react with the cyanide. If a ferro-nickel is being analyzed a stronger solution of KCN should be used.

Such elements as vanadium, chromium, tungsten, molybdenum or manganese do not interfere even when present in large amounts in the sample.

References:

Johnson, "Chemical Analysis of Special Steels, Alloys and Graphites."

Grossman, *Chem. Ztg.*, XXXIV, 673.

Jamieson, *J. Am. Chem. Soc.*, XXXII, 757.

Boyle, *Chem. Eng.*, XIV, 288.

The Dimethylglyoxime Method for Nickel

This is a very accurate and fairly rapid method. Copper and cobalt if present do not interfere and for this reason steels containing more than traces of copper or cobalt should be analyzed by this method. In cases of dispute umpire analyses should be made in this way.

From faintly ammoniacal solution dimethylglyoxime precipitates nickel promptly and completely as a voluminous red compound, nickel dimethylglyoxime, which is soluble in acid solutions. The precipitate has the composition $(CH_3)_2C_2(NOH)_2Ni(CH_3)_2C_2(NO)_2$ and when dried at 115°C. contains 20.32 per cent. nickel.

For use the dimethylglyoxime ($CH_3CNOHCNOHCH_3$) is dissolved in alcohol, 1 gram to 100 c.c. Since the precipitate is distinctly soluble in a solution containing more than 50 per cent. of alcohol the volume of the

solution to which the alcoholic dimethylglyoxime is added should be greater than that of the alcoholic solution.

Method of Analysis.—Treat the sample exactly as was directed for the cyanide determination of nickel until the ammonia is added to the solution containing citric acid. As soon as the solution becomes alkaline add acetic acid until it is acid and then heat to boiling. Now add about 20 c.c. of the dimethylglyoxime solution or five times as much dimethylglyoxime as there is nickel present. Then add ammonia until the solution smells slightly of ammonia or reacts alkaline. While still hot filter on a weighed Gooch crucible, wash well, dry at 110–120°C. for 45 minutes and weigh. Multiply the weight by 0.2032 to get the weight of the nickel.

Notes on the Process.—The nickel dimethylglyoxime sublimes at 250°C., hence it should not be heated too long and too hot.

In the precipitation large amounts of ammonium salts do no harm but an excess of ammonia tends to prevent the formation of the precipitate.

If cobalt be present in considerable amount the solution should be diluted to 100 c.c. for every 0.10 gram of cobalt.

The dimethylglyoxime method when properly modified to suit the samples makes an excellent method to determine the nickel in ores.

The reagent is expensive. It may be recovered by mixing the nickel salt to a paste with water, warming with potassium cyanide, filtering hot and precipitating the oxime with acetic acid.

High silicon steels should have the silicon removed before precipitating the nickel. If the nickel content is less than 0.100 per cent. it is best to carry out the ether separation for nickel as given on page 154.

References:

Brunk, *Z. angew. Chem.*, XX, 834.

Ibbotson, *Chem. News*, CIV, 224.

Parr and Lindgren, *Trans.* Am. Brass Founders Assoc., V, 120, describe a method for titrating the nickel dimethylglyoxime.

The Determination of Cobalt in Steel

Cobalt is present to some extent in all samples of iron and steel that contain nickel. It is now being intentionally introduced into some varieties of high-speed steel.

Cobalt is separated from most of the iron in a hydrochloric acid solu-

tion by means of the ether separation, along with nickel, manganese, copper, vanadium, aluminum and chromium. In this solution the nickel and cobalt are separated from the other elements by means of hydrogen sulfide. If cobalt is present in small amounts it is best separated from the nickel by Ilinsky and Knorre's reagent (nitroso-β-naphthol). If present in large amounts it is best to deposit the cobalt and nickel together electrolytically and then dissolve the deposit and precipitate the nickel with dimethylglyoxime.

Process of Analysis.—Dissolve 1 to 5 grams of the sample in 30 c.c. of HCl, sp. gr. 1.1. When dissolved add a few drops of HF, warm, and add gradually 1 or 2 c.c. of HNO_3 to oxidize the iron. Then carry out the ether separation as directed under vanadium on page 154, until the ether has all been boiled off. Heat to boiling and precipitate copper with H_2S, filter and wash. Add sodium carbonate to the filtrate until the solution is alkaline, then acetic acid until it is faintly acid, then 5 grams of sodium acetate, dilute to 100 c.c., heat to 70° and pass H_2S through solution for one hour. Filter through a filter paper on which has been packed macerated filter paper and wash with a 4 per cent. HCl solution saturated with H_2S to remove all manganese sulfide. The filtrate should be tested for cobalt. Ignite the precipitate until all the paper has been burned off.

Dissolve the precipitate in strong HCl and a little HNO_3, add 5 c.c. of H_2SO_4 and evaporate until fumes of H_2SO_4 appear. The procedure from this point depends upon whether the cobalt is present in large or small amounts.

If cobalt is present in amount less than 2 or 3 per cent., dilute the solution to 100 c.c., add 10 c.c. of concentrated HCl and a sufficient amount of nitroso-β-naphthol solution. Allow the precipitate to settle for several hours, filter, wash with a hot 10 per cent. HCl solution, then with water until the acid is removed. Ignite the precipitate until the carbon is all burned off, cool the crucible, dissolve the cobalt oxide in HCl, add H_2SO_4, evaporate to dryness, and ignite to a low red heat, and weigh the cobalt as $CoSO_4$ containing 38.04 per cent. cobalt.

If the cobalt is present in large amounts precipitate it with the nickel as follows: Neutralize the sulfuric acid solution of cobalt and nickel obtained above with NH_4OH and add 30 c.c. of NH_4OH, sp. gr. 0.90, in excess, dilute to 100 c.c. and electrolize

the solution using a gauze cathode and a current of 2 amperes. Deposition should be complete in one hour. To test the completeness of the deposition withdraw a few drops of the solution by means of a pipette and add it to a drop of $(NH_4)_2S$ on a white plate. If no brown color appears the deposition is complete. Remove the cathode, wash with pure water, rinse with alcohol, dry at 105° and weigh the cobalt plus nickel. Dissolve the precipitated metals in strong HCl, dilute to 100 c.c., and precipitate any nickel that may be present as directed under the dimethylglyoxime method. Subtract the weight of the nickel from the combined weights of the nickel and cobalt.

Nitroso-β-naphthol Solution.—Dissolve 8 grams of the solid in 300 c.c. of cold glacial acetic acid and dilute with 300 c.c. of water. The solution should be made fresh each month.

Notes on the Process.—The separation of cobalt and nickel from manganese and iron by precipitation from a weakly acid solution must be carried out carefully as some of the cobalt and nickel will escape precipitation if the solution is too acid and some manganese will precipitate if the solution is too nearly neutral. The filtrate should be tested as follows: evaporate to 50 c.c., add an excess of $(NH_4)_2S$, acidify with an excess of acetic acid and warm the solution. If nickel or cobalt be present a precipitate will remain.

Nitroso-β-naphthol also precipitates copper, chromium and iron but does not precipitate aluminium, lead, cadmium, manganese, nickel, mercury, and zinc.

The cobalt nitroso-β-naphthol precipitate is very voluminous, hence it is not advisable to precipitate large amounts of cobalt in this way. Its formula is $[C_{10}H_6O(NO)]_3Co$.

The cobalt precipitate may be ignited in a Rose crucible with oxalic acid until all the carbon is burned off and finally reduced to metal by igniting in a current of hydrogen. It is difficult to eliminate all of the carbon.

The nickel may be determined in the filtrate from the cobalt by evaporating with 10 c.c. of H_2SO_4 to destroy the nitroso-β-naphthol and precipitating with dimethylglyoxime or KOH and bromine.

The electrolytic deposit of cobalt is generally brown or black and the results tend to be a trifle high. If too small an amount of NH_4OH is used some nickel or cobalt oxide may deposit on the anode, while too large an amount retards the deposition of the metals. Nitrates should be absent.

Nickel and cobalt also precipitate well electrolytically from solutions of cyanides, oxalates, and in the presence of alkaline acetates, tartrates, citrates and phosphates.

References:

Funk, *Z. anal. Chem.*, 45, 562 (1906). Sulfide precipitation.
Ilinsky and Knorre, *Ber.*, 18, 699, 2728 (1885). Nitroso-β-naphthol.
Copaux, *Chem. News*, 87, 291 (1903). Nitroso-β-naphthol method.
Smith, "Electro-analysis," 122.
Mellor, "Quantitative Inorganic Analysis," 389, 394.

CHAPTER X

THE DETERMINATION OF VANADIUM IN STEEL

Very small amounts of vanadium in steel seem to profoundly alter some of the properties of the metal. Hence it has become necessary to be able to determine the vanadium very accurately. In all cases, however, when the analysis shows the presence of very small percentages of vanadium the quantitative results should be confirmed by a qualitative test. The test is given on page 156.

The Manganese Dioxide-permanganate Method

The following method gives very good results and no element present in steel interferes. It depends upon the selective oxidation of ferrous sulfate in the presence of vanadyl sulfate by manganese dioxide. The vanadyl sulfate is titrated by adding an excess of standard permanganate, the excess being titrated by sodium arsenite.

The reactions are:

$$2H_3VO_4+2FeSO_4+3H_2SO_4=V_2O_2(SO_4)_2+Fe_2(SO_4)_3+6H_2O.$$

$$2FeSO_4+MnO_2+2H_2SO_4=Fe_2(SO_4)_3+MnSO_4+2H_2O.$$

$$5V_2O_2(SO_4)_2+2KMnO_4+22H_2O=10H_3VO_4+K_2SO_4+2MnSO_4+7H_2SO_4.$$

It is essential that the manganese dioxide be of the natural or crystalline variety (pyrolusite) and that it be not too fine. It should pass through a 120-mesh sieve, and yet settle in a beaker of water in 15 seconds. The fine precipitated variety will oxidize $V_2O_2(SO_4)_2$.

Process of Analysis.—In a 500 c.c. flask a 2-gram sample of the steel or iron is dissolved in a mixture of 50 c.c. of water and 12 c.c. concentrated H_2SO_4 with application of heat. Then 1 c.c. of HNO_3 (sp. gr. 1.42) is added cautiously to oxidize the iron and the solution is boiled for a few minutes to remove the nitrous fumes. Then the solution is diluted with 30 c.c. of water, 5 c.c. of phosphoric acid and a strong solution of $KMnO_4$ is added to completely oxidize all carbon, etc., and the solution is

boiled. If the permanganate or the resulting MnO_2 should disappear, not enough permanganate has been used, and more should be added. Now ferrous sulfate is added to reduce the MnO_2, $HMnO_4$, H_2CrO_4, H_3VO_4, etc., and the solution is again boiled to remove any possible nitrous fumes. Then distilled water is added to make the volume about 250 c.c., N/10 $KMnO_4$ added until the solution is pink, and the solution cooled to tap water temperature. Ferrous sulfate solution is now added until all reducible compounds, including chromic and vanadic acids, are reduced. Only enough ferrous sulfate should be added to be certain that there is a decided excess present. A solution, 1 c.c. of which is equal to about 0.01 gram of iron, is the one used. Now about 1 gram of C.P. MnO_2 is added and the solution shaken vigorously. After two minutes a drop is tested with ferricyanide on a white plate to see if the iron is completely oxidized. It generally takes from four to six minutes. At the end of each minute the solution is tested for ferrous iron until none is present and the shaking is continued for about one-half minute longer. It should be noted that a bluish color will always be obtained in the presence of vanadyl sulfate after the test drop has stood for a few seconds. The end should be taken when the test does not show blue immediately. The blue color which forms after a few seconds, even when there is no ferrous iron present, is due to the reduction of ferri- to ferrocyanide by the vanadyl sulfate. One can become familiar with this end point by adding a drop of ferric sulfate containing vanadyl sulfate to a drop of ferricyanide on a white plate.

The MnO_2 oxidizes the ferrous sulfate to ferric sulfate, but does not oxidize the vanadyl sulfate ($V_2O_2(SO_4)_2$). Then the MnO_2 is filtered off on an asbestos mat, using suction. From a burette a standard solution of $KMnO_4$ is added until a pink tinge is present in the solution, then 1 c.c. more is added and the solution shaken and after one minute the excess permanganate is titrated with Na_3AsO_3 solution. The end point is very sharp. If at this point the operator is not satisfied with this titration, the excess arsenite may be oxidized with $KMnO_4$, ferrous sulfate again added, then oxidized with MnO_2 as before, and the titration repeated, thus giving a check on the titration. A blank determination must be run on a vanadium-free steel, and

the result deducted. The blank generally amounts to about 0.00075 gram V. The time required is about one-half hour and the results are very satisfactory. In fact the accuracy is nearly that of a phosphorus determination.

The vanadium steel standard furnished by the Bureau of Standards was analyzed by the above method. The result of the Bureau chemists is 0.143 per cent. V and the average of the cooperating chemists is 0.15 per cent. V. The writer obtains the following results, the average being 0.143 per cent.:

0.140	0.138
0.147	0.147
0.143	0.143

To further test the method, 2-gram samples of vanadium-free steel with the addition of ferrovanadium containing 0.00684 gram of vanadium were analyzed. The results were 0.00680 and 0.00690 gram V. Another sample with 0.0342 gram V was analyzed, and 0.03432 gram V was found.

To test the effect of chromium on the method, the Bureau of Standards' sample above mentioned was analyzed with the addition of 0.100 gram Cr. The results were 0.143 per cent. and 0.143 per cent. V, showing that chromium has no effect on the vanadium results. Scores of other determinations have been made, proving the accuracy of the method.

The $KMnO_4$ solution used equals 0.001 gram iron per cubic centimeter and the arsenite solution has the same strength. This makes the $KMnO_4$ equal 0.000914 gram vanadium per cubic centimeter. The arsenite solution is made by dissolving about 1.78 gram As_2O_3 in Na_2CO_3 solution and diluting to 2000 c.c. as directed on page 85.

Notes on the Process.—The ferricyanide solution should contain about 10 per cent. hydrochloric acid. The phosphoric acid is used to discharge the color of the iron so as to make the end point sharp. It is added at the time directed in order that any impurities in the acid may be oxidized. If the amount of vanadium in the sample is very low, a larger sample should be used with a corresponding increase of phosphoric acid.

The MnO_2 may be used over and over. As the finer particles become dissolved the dioxide becomes slower in action.

Ferrous sulfate must not be used in the titration as it gives an in-

distinct end point due to slight reduction of vanadium along with permanganate.

References:
Demorest, *J. Ind. Eng. Chem.*, IV, April, 1912.

Determination of Vanadium in Ferrovanadium

Ferrovanadium may contain as much as 50 per cent. of vanadium. Since it is very subject to segregation care must be taken to get a properly representative sample. It is best to make several determinations and average the results.

Weigh 0.50 gram of the finely crushed sample and place in a 750 c.c. flask. Dissolve with 50 c.c. of water and 15 c.c. of sulfuric acid using heat. When the sample is dissolved add 2 c.c. of nitric acid and boil to expel nitrous fumes. Then add strong permanganate solution until the liquid remains pink when boiled. Add a little water to cool the solution somewhat, then add ferrous sulfate solution until all MnO_2 is dissolved and boil vigorously to expel any nitrous acid formed by the action of the ferrous sulfate on the nitric acid. Now add permanganate enough to color the solution pink and cool to tap water temperature. Dilute to 400 c.c. and run in ferrous sulfate until all yellow tints are gone from the liquid and it becomes blue due to the presence of vanadyl sulfate. Then add about 10 c.c. more so that there is an excess of ferrous sulfate present. Now add 2 grams of MnO_2 (preferably some which has been used before or has been shaken with ferrous sulfate and dilute sulfuric acid to dissolve the fine particles). Shake the flask vigorously and test the solution for ferrous ions after each minute. As soon as a test is obtained which does not show blue *immediately*, cease shaking, filter off the MnO_2 and titrate the vanadium with permanganate solution of about N/10 strength. Add the permanganate until a pink tinge is obtained which does not go after shaking the solution a minute, then add a few drops more and titrate back with a standard arsenite solution.

If it is desired to check the titration, add ferrous sulfate solution again, then add MnO_2 and repeat the oxidation of the ferrous sulfate and the titration.

When there is a large amount of vanadyl sulfate present the

test for ferrous ions with ferricyanide must be observed immediately as the vanadyl sulfate will quickly reduce the ferricyanide to ferrocyanide and the test will turn blue.

The ferrovanadium may easily be crushed by folding it in several thicknesses of paper and hammering on an anvil. The ferrovanadium is then separated from paper and dirt by means of a magnet.

The above method gives very satisfactory results for either vanadium steels or ferrovanadiums. No elements interfere. The chief points to attend to are to make sure that all oxidizable elements are oxidized by the permanganate in hot solution and all nitrous fumes are removed by boiling, and that the MnO_2 used is of the right kind. It must be crystalline and free from all excessively fine particles. The MnO_2 should be washed with running water until it settles perfectly clear in 15 seconds when stirred up in a large beaker.

Determination of Chromium and Vanadium

Process of Analysis.—Dissolve the proper amount of sample in 50 c.c. of water, 12 c.c. of sulfuric acid and 15 c.c. of nitric acid. When the sample is all dissolved, boil to remove oxides of nitrogen, then add 50 c.c. of water and strong permanganate solution until an excess is present and a precipitate of MnO_2 remains after 20 or more minutes' boiling. The addition of permanganate is to oxidize all carbon, etc., and the long boiling is to decompose the permanganate excess. If the permanganate is not all destroyed by the boiling, the result for chromium will be too high.

After the permanganate is all destroyed cool the solution somewhat and filter through an asbestos mat and wash a few times. Dilute the filtrate to 300 c.c., add 30 c.c. of 1 :3 sulfuric acid and titrate.

To titrate, run in the standard ferrous sulfate solution (N/50) until all brown tints are gone, indicating complete reduction of the chromic and vanadic acids to chromium and vanadyl sulfates, then add several cubic centimeters more. To make sure that enough ferrous sulfate has been added one may test a drop of the solution with ferricyanide on a porcelain plate. Now add the standard permanganate solution (N/50) until a pink color

is obtained which remains after a minute of stirring of the solution. Then add a cubic centimeter more and titrate the excess of permanganate with the arsenite solution. The iron value of the permanganate used subtracted from the iron value of the total amount of ferrous sulfate and arsenite multiplied by 0.310 gives the amount of chromium present.

Now add sufficient ferrous sulfate to the solution to reduce the probable amount of vanadium present, add a gram or two of the prepared MnO_2 and shake the flask until a test with ferricyanide on a white plate shows that all the ferrous sulfate is oxidized, filter and titrate the vanadium with standard permanganate as directed under the method for vanadium alone.

Notes on the Process.—A blank must be run on the chromium (as well as on the vanadium) by treating a chromium and vanadium-free sample. After the permanganate has been used in the hot solution to oxidize all carbon, etc., the excess is decomposed by boiling. However, there is always a minute trace of the MnO_2 (or higher oxide) left in solution which cannot be filtered out, and this is reduced when the ferrous sulfate is added to titrate the chromium. Hence, the necessity to run a blank on the chromium. This blank is very constant if the boiling is always carried on the same length of time.

The reactions involved in the titrations are as follows:

On addition of ferrous sulfate,

$$2H_2CrO_4+6FeSO_4+6H_2SO_4=Cr_2(SO_4)_3+3Fe_2(SO_4)_3+8H_2O, \text{ and}$$
$$2H_2VO_4+2FeSO_4+3H_2SO_4=V_2O_2(SO_4)_2+Fe_2(SO_4)_3+5H_2O.$$

When the permanganate is added only the vanadyl sulfate is oxidized thus,

$$5V_2O_2(SO_4)_2+2KMnO_4+22H_2O=10H_3VO_4+K_2SO_4+2MnSO_4+7H_2SO_4.$$

So, if the ferrous sulfate and arsenite solutions are equal cubic centimeter for cubic centimeter to the permanganate, the number of cubic centimeters of ferrous sulfate plus arsenite used minus the number of cubic centimeters of permanganate used to oxidize back the vanadium is the number of cubic centimeters of ferrous sulfate required to reduce the chromium from the hexavalent to the trivalent state. Since the chromium is reduced three valences and the iron is oxidized simultaneously one valence it requires three atoms of iron to reduce one atom of chromium and therefore the iron value of the ferrous sulfate used multi-

plied by $\frac{52}{3\times55.84}$ gives the amount of chromium present. Since the vanadium is only changed by one valence by the permanganate, the iron value of the permanganate used multiplied by $\frac{51.06}{55.84}$ gives the amount of the vanadium present. These fractions figure out to be 0.3103 and 0.915 respectively. If the solutions used are fiftieth normal their values are $\frac{52}{3\times50\times1000}$ or 0.0003466 gram per cubic centimeter for chromium and $\frac{51.06}{50\times1000}$ or 0.001021 gram of vanadium per cubic centimeter.

Johnson's Method for Chromium and Vanadium

This method is quick and fairly accurate though results tend to run a trifle low. Vanadium and chromium are determined together practically as quickly as either one.

Vanadium and chromium are oxidized by permanganate to vanadic and chromic acids respectively. Then standard ferrous sulfate reduces them to vanadyl sulfate and chromium sulfate, and standard permanganate added to the cold dilute solution oxidizes the vanadium only back to vanadic acid. If the standard solutions are equal to each other cubic centimeter for cubic centimeter, the ferrous sulfate minus the permanganate equals the ferrous sulfate required to titrate the chromium. Then, if a little potassium ferricyanide is put in the solution the vanadium may be titrated by ferrous sulfate and when the vanadic acid is all reduced any ferrous sulfate added in excess will give a blue color with the ferricyanide.

Process of Analysis.—Dissolve 2 grams of steel in 50 c.c. of water and 10 c.c. of sulfuric acid in a 500 c.c. beaker. When the action is over, add 60 c.c. of 1.2 sp. gr. nitric acid to oxidize the iron and boil two minutes. Then add 200 c.c. of water and add a strong permanganate solution a little at a time until a slight precipitate of MnO_2 is obtained that does not dissolve on boiling 20 minutes. Now cool and filter through a Gooch mat and wash several times with dilute sulfuric acid.

Return the filtrate and washings to the beaker and add 30 c.c. of 1.3 sulfuric acid. The volume should now be made about 350 c.c. and the solution is ready to be titrated.

Add a ferrous sulfate solution of about a fiftieth normal strength until the fluid in the beaker loses all brown tints and

assumes a practically colorless shade in plain vanadium steels or a green color in chrome steels. Then add a few more cubic centimeters to make sure enough has been added. Now add one-fiftieth normal permanganate solution slowly and with vigorous agitation of the solution until a very faint pink is obtained that persists after 30 seconds' stirring. Should even as much as 5 or 6 per cent. of chromium be present a practiced operator can easily detect the pink tints through the chrome green. The amount of ferrous sulfate and permanganate used should be recorded if the amount of chromium is desired to be known. The iron value of the ferrous sulfate minus the iron value of the permanganate multiplied by 0.3103 gives the amount of chromium.

The solution is now ready for the vanadium titration. Add 1 c.c. of a 0.1 per cent. solution of potassium ferricyanide (always use the same amount) and drop in slowly, and with stirring, the standard ferrous sulfate until a drop produces a green color free from yellow tints. If much chromium is present the ferrous sulfate is added until the green chromium color begins to darken. It is well to add from time to time during the titration a drop of the indicator and see if a green coloration is produced at the point where the drop mixes with the solution. The iron value of the ferrous sulfate multiplied by 0.914 gives the amount of vanadium present.

A blank must be run on a steel free from vanadium but otherwise of similar composition. Also, it is best to run at the same time a vanadium determination on a steel containing a known amount of vanadium.

Notes on the Process.—The presence of chromium increases the blank. If copper is present it will precipitate out when the ferricyanide is added. In such a case the ferricyanide is added before the MnO_2 is filtered off and the copper ferricyanide filtered off with the MnO_2. If a further precipitate is produced when the ferricyanide is added for the titration, another determination is run using double the amount of ferricyanide to precipitate the copper. Nickel, if present, will also slowly precipitate with the ferricyanide. Molybdenum does not interfere. If the sample is a tungsten steel, when it is dissolved it should be digested until the precipitated tungstic acid is a bright yellow. Then enough permanganate should be added to cause the precipitate of tungstic acid to be colored chocolate by the MnO_2 formed.

Ferrovanadium is analyzed as a steel except that a smaller sample is used (0.5 gram). To titrate, ferricyanide indicator is added, then ferrous sulfate until the light blue of the vanadyl salt is darkened slightly. The amount of ferrous sulfate is noted, then standard permanganate is added until a rose tint is obtained. From the amounts of permanganate and ferrous sulfate used, the vanadium and chromium are calculated. The vanadium present is obtained by multiplying the iron value of the permanganate used by 0.914. The chromium is obtained by subtracting the iron value of the permanganate from the iron value of the ferrous sulfate used and multiplying by 0.3103. The permanganate used should be about N/10.

It is absolutely essential in vanadium and chromium titrations when coming back with permanganate to add the permanganate until three drops give a faint pink which remains visible after 30 seconds' stirring. The ferrous sulfate should be added until three drops produce a distinct darkening of the green but not a blue. A better way is to add an excess of permanganate and titrate the excess with arsenite.

Ferrovanadium containing much silicon may dissolve very difficultly. After as much has dissolved as will in sulfuric and nitric acid a cubic centimeter of hydrofluoric acid should be added and the solution evaporated to fumes to expel the hydrofluoric acid.

References:

Johnson, "Chemical Analysis of Special Steels, Steel Making Alloys and Graphites."

Crites, *J. Ind. Eng. Chem.*, III, 574.

Method of Cain and Hostetter for Vanadium

It has long been known that when ammonium phosphomolybdate is precipitated from a solution containing vanadium the precipitate carries down with it vanadium and has a brick red color. Cain and Hostetter have shown that under the proper conditions the vanadium is completely precipitated, although it is not precipitated at all with molybdic acid alone.

Moreover, Cain and Hostetter have shown that after the precipitate is dissolved in concentrated sulfuric acid the vanadium is reduced in the concentrated acid solution to vanadyl sulfate, that is, to tetravalent vanadium, by means of hydrogen peroxide. The excess of peroxide is driven off by heating the solution until the sulfuric acid fumes strongly. Then the solution is diluted and the vanadium titrated to vanadic acid (pentavalent vanadium) by standard permanganate solution.

The method is especially valuable when determining vanadium in

materials containing a very small percentage of vanadium, as samples as large as even 50 grams may be used. Furthermore, the method has the very great advantage of affording qualitative confirmation of the presence of vanadium.

Process of Analysis.—For steels containing vanadium, chromium, nickel, titanium, manganese, molybdenum, singly or in combination, dissolve an amount of drillings estimated to contain 2 to 10 mg. of vanadium in nitric acid (sp. gr. 1.135), boil till free from fumes, oxidize with permanganate solution, dissolve the manganese dioxide with potassium nitrite solution, and boil till free from fumes. In other words, prepare the solution exactly as for a phosphorus determination, examining any insoluble residue for vanadium. Nearly neutralize with NH_4OH (0.96) and add an amount of sodium phosphate solution containing at least ten times as much phosphorus as there is vanadium present. Bring the solution to boiling, remove from the plate and add at once the usual necessary excess of the molybdate reagent to precipitate the amount of phosphoric acid added. Agitate for a minute or so, when it will be found that the precipitate settles rapidly. Filter the supernatant liquid by suction through an asbestos filter, and wash three times by decantation with hot acid ammonium sulfate solution, pouring the washing liquid through the filter. The last wash solution should be decanted off as completely as possible from the precipitate in the flask and the filter should be sucked dry. Fit the rubber stopper carrying the filter funnel to a small, dry bottle and pour hot, concentrated sulfuric acid on the filter to dissolve the small amount of precipitate thereon. This dissolves quickly and the solution is drawn through by suction into the bottle. Transfer the contents of the bottle to the flask in which precipitation was made, wash the bottle once with concentrated sulfuric acid, adding the washings to the flask. For every 10 mg. of phosphorus present a final volume of 5 to 8 c.c. of concentrated sulfuric acid is necessary. Heat the contents of the flask until solution takes place, add a few drops of nitric acid (1 :25), and when fumes are coming off strongly remove the flask from the plate, cool and reduce the vanadium by successive small additions of hydrogen peroxide. Replace on the hot plate, fume for four or five minutes, cover the flask, cool, dilute so as to secure an acidity of one part to

five by volume, and titrate at a temperature of 70° to 80°C. with 0.01 N permanganate. The condition as to acidity and temperature must be closely observed in order to secure a satisfactory end point.

For steels of the above classes containing tungsten, the only change necessary is to dissolve in aqua regia, dilute with hot water, filter off the tungstic acid, nearly neutralize with NH_4OH, and add 10 grams solid ammonium nitrate for every 100 c.c. of the final volume before precipitating as above described. If desired, the tungstic acid on the filter may be dissolved in a small amount of sodium hydroxide solution (free from vanadium), acidified with nitric acid and tested for vanadium with hydrogen peroxide.

Notes on the Process.—The presence of vanadium in the phosphomolybdate precipitate is shown by the yellow to orange color of the cold, concentrated sulfuric acid solution of the precipitate, as little as 0.05 mg. of vanadium showing a color in a volume of 25 c.c.

In carrying out the reduction of the vanadium by peroxide it is necessary to use a flask rather than an open beaker. If the latter is used, the molybdenum is reduced where the solution creeps up the sides of the beaker. The hydrogen peroxide is added in small quantities to the cold, concentrated acid solution with agitation of the solution, until the solution takes on a deep brown color owing to action on the molybdate. This brown disappears on heating and is followed by the clear greenish-blue of vanadyl sulfate.

All nitric acid must be removed by heating the solution to dense fumes before reducing by peroxide. Nitrous fumes easily oxidize tetravalent vanadium to the pentavalent state.

The time required is about a half hour on ordinary steels. The alloy steels, such as tungsten steel, require more time in order to get them completely dissolved and oxidized. The method can be used for ores as well as metals.

If the volume of the solution from which the precipitate is made is very large and especially if there is hydrochloric acid present, it is best to add 10 grams of ammonium nitrate to each 100 c.c. Potassium nitrate or nitric acid solutions should not be used to wash the precipitate as it is more or less soluble in them. Also the temperature of precipitation should be high as directed.

Reference:

Cain and Hostetter, *J. Am. Chem. Soc.*, IV, 250.

Peroxide Reduction Method for FerrovaNadium

The writer has made use of the discovery of Cain and Hostetter that hydrogen peroxide (or alkali peroxide) reduces vanadic acid in strong sulfuric acid solution to determine the vanadium in ferrovanadium.

The process is as follows: Dissolve ½ gram of the sample in 30 c.c. of water and 15 c.c. of sulfuric acid. When action ceases add 5 c.c. of nitric acid and boil until all nitrous fumes are expelled, then add potassium permanganate solution until an excess is present. Evaporate to fumes of sulfuric acid and fume heavily for several minutes to expel all nitric acid. Cool and add 10 c.c. of hydrogen peroxide ("Dioxygen" is good). Evaporate to fumes of sulfuric acid, cool and add 5 c.c. more of hydrogen peroxide and evaporate to fumes again (the liquid has a great tendency to "bump"). Continue the heating until heavy billows of fumes have been filling the flask for about four minutes. Cool the solution and add 100 c.c. of water and heat until all soluble salts are dissolved and the solution is clear. This takes considerable heating and stirring. Now dilute to 300 c.c. with cold water and titrate with N/10 permanganate until the solution takes on a pink tinge which does not disappear on stirring. Then add a few drops more and shake and titrate the excess of permanganate with N/10 sodium arsenite solution. The number of cubic centimeters of permanganate used minus the number of cubic centimeters of arsenite used multiplied by 0.005106 gives the amount of vanadium present.

Ether Separation Method for Vanadium

The following method for vanadium is very accurate and should be used in important cases.

It depends upon the fact that when a solution of ferric chloride in HCl is shaken up with sulphuric ether most of the iron will go into the ethereal solution while the chlorides of vanadium, nickel, copper, manganese, cobalt, chromium and aluminum remain entirely in the aqueous solution. The conditions for securing a good separation are as follows: first, the chlorides must be dissolved in HCl of between sp. gr. 1.1 and 1.13; second, the volume of the solution must be small, not exceeding 50 c.c.; and third, the ether must be free from alcohol and must be saturated with HCl by previously shaking it up

with 5 to 10 c.c. of the concentrated acid. Finally, sulphates are said to interfere with the ether separation and if present, as is sometimes the case in applying the process to ores, must be removed. In this case the iron can be precipitated by NH_4OH and then dissolved in HCl and the ether separation applied to this solution. Part of the nickel will be in the filtrate from the iron.

Process.—Dissolve 5 grams of the drillings in 30 c.c. of dilute HCl (1.1) in a small covered beaker. When dissolved, add a few drops of HF, warm, and add gradually 1 or 2 c.c. of HNO_3 to oxidize the iron. Evaporate the solution to about 10 c.c. Cool it and pour it into a separatory funnel of about 150 c.c. capacity, having a very short stem. Wash out the beaker with warm HCl of 1.13 sp. gr., transferring all the solution to the funnel. To keep the volume small, use successive small portions of 5 or 6 c.c. of the acid in washing. The total volume of the solution in the funnel should not exceed 40 c.c. Now cool the funnel and its contents and cautiously add 45 to 50 c.c. of ether previously saturated with HCl. Put in the stopper and shake the funnel vigorously for five minutes, keeping it cool by holding it under running water from the tap. Set the funnel in a rack and let it stand until the ether separates and the line between the two layers of liquid is sharp. Then take out the stopper carefully and draw off the aqueous solution down to the stop-cock, being careful to empty the tube. Now add 5 or 6 c.c. of HCl, sp. gr. 1.13, to the ether in the funnel and shake it again. Let it separate as before and draw off the acid, adding this to the first extract. It is desirable to use as little acid as possible in the washing as it takes up some iron from the ether and increases that to be subsequently removed from the aqueous solution.

During the whole operation the ether and the funnel should feel cool to the hand; if allowed to become too warm, the vapor pressure may blow the stopper out of the funnel. The aqueous solution contains some dissolved ether, a little ferric chloride (which should not exceed 2 per cent. of that in the original solution) and the whole of the chlorides of vanadium, nickel, cobalt, manganese, aluminum and copper. Set the flask containing this solution on a water bath or hot plate and heat it until the ether is expelled.

Reduce to small volume in a casserole and remove the hydro-

chloric acid completely by evaporation to dryness with concentrated nitric acid. Take up in strong nitric acid, dilute with water, nearly neutralize with sodium hydroxide solution and pour slowly into 150–200 c.c. of 10 per cent. sodium hydroxide solution, with vigorous stirring. Filter, retain filtrate and repeat the sodium hydroxide treatment twice with the insoluble material, dissolving it each time in dilute nitric acid. In these latter treatments the volume of sodium hydroxide solution may be smaller. The filtrates now contain the vanadium. They are combined and made nearly neutral or faintly alkaline to litmus paper by cautiously adding dilute nitric acid. Precipitate the vanadium by an excess of fresh mercurous nitrate solution. The mercurous vanadate is filtered after a short digestion on the steam bath, washed with 1 per cent. mercurous nitrate solution (the filtrate being tested by adding more mercurous nitrate solution and digesting) and the filter paper burned off in a platinum crucible with consequent volatilization of the mercury. The impure vanadium pentoxide remaining is fused with a little sodium carbonate, extracted with water, the extract filtered, in order to get rid of the small amounts of iron which sometimes contaminate the vanadium pentoxide at this point, and the precipitation with mercurous nitrate repeated. A further fusion and precipitation may be necessary. The vanadium pentoxide is now practically pure and is fused with sodium carbonate. It is then dissolved in 25 c.c. of 1 : 1 H_2SO_4, diluted to 150 c.c. and a stream of sulfur dioxide is passed through the boiling hot solution, which is then boiled until the SO_2 is all removed and titrated hot with permanganate.

For the cadmium carbonate method recommended by the U. S. Bureau of Standards see Reprint 161.

Qualitative Tests for Vanadium (and Titanium)

The color of the phospho-molybdate dissolved in strong sulfuric acid, according to Cain and Hostetter, affords a good qualitative indication of the presence or absence of vanadium. The following test, elaborated by Johnson, also is good. It depends upon the fact that in dilute acid solutions hydrogen peroxide produces a brick red color with vanadium, due to the formation of pervanadic acid. Titanium under the same conditions causes a yellow color when the peroxide is added. If both

vanadium and titanium are present a mixed color is obtained. If a clear yellow is obtained on adding the peroxide only titanium is present, but if a reddish color is obtained both may be present. If ferrous sulfate is added to the solution after the hydrogen peroxide the reddish color of the vanadium disappears first, leaving the yellow of the titanium.

Procedure.—Dissolve 0.5 gram of the sample in 10 c.c. of 1:3 sulfuric acid, heating until action ceases. Add 5 c.c. of concentrated nitric acid and boil until red fumes are all gone. If tungsten be present, filter. Pour half of the solution into each one of two 6-in. test-tubes. Then add to one tube 5 c.c. of water and to the other 5 c.c. of a 3 per cent. solution of hydrogen peroxide. If vanadium be present the tube to which the peroxide was added will be distinctly redder than the other, even if there be only a few hundredths per cent. of vanadium in the sample. If titanium but no vanadium be present the color will be a clear yellow. If a red color is produced vanadium, and possibly titanium, is present. Add N/20 ferrous sulfate 1 c.c. at a time, shaking after each addition, until red color gradually fades. If titanium be present the red will change to a clear yellow. If none be present the red will gradually fade out without changing to yellow.

CHAPTER XI

THE DETERMINATION OF TUNGSTEN, CHROMIUM, AND SILICON IN STEEL

Tungsten may be found in steel in amounts up to 25 per cent. and is generally accompanied by chromium up to as high as 6 per cent.

When a steel containing tungsten is dissolved in a mixture of nitric and hydrochloric acids and the solution is evaporated to dryness and the residue treated with hydrochloric acid, the tungsten is left insoluble as WO_3 with the SiO_2. In order to render the WO_3 entirely insoluble more than one evaporation to dryness is necessary. When the residue is treated with sulfuric and hydrofluoric acids the silica is driven off while the tungstic anhydride is left behind. The tungstic anhydride is always contaminated with ferric oxide and must be purified for perfect results.

The chromium in the filtrate is oxidized to chromic acid and titrated with ferrous sulfate.

The tungsten is usually and best determined gravimetrically by weighing as WO_3, but since the WO_3 is an acid anhydride it may be determined volumetrically by titrating with a standard alkali solution.

Tungsten steels are very hard and difficult to drill. If they are annealed at 750°C. for a couple of hours they will become soft enough to drill.[1]

Process of Analysis.—Place 2 grams of the drillings in a 200 c.c. casserole and add 40 c.c. of hydrochloric acid, sp. gr. 1.19, and heat nearly to boiling. When action ceases, add from time to time a few drops of nitric acid until the steel is entirely decomposed. In this way the sample is dissolved without the separation of WO_3. When decomposition is complete add 5 c.c. HNO_3, boil the solution down to about 10 c.c., add 50 c.c. of water, boil for several minutes and filter. Wash well with a hot 5 per cent. HCl solution until all ferric chloride is removed. Evaporate the filtrate to hard dryness, add 15 c.c. of strong HCl and heat until all iron salts are dissolved, dilute to 50 c.c., heat to boiling and filter, wash well to wash out all iron. Ignite the two papers and

[1] Johnson, "Chemical Analysis of Special Steels, Etc.," p. 197.

their contents in a platinum crucible until all paper is burned off, but do not heat the WO_3 hotter than a dull red. Cool in a desiccator and weigh.

Add three drops of sulfuric acid and 5 c.c. of hydrofluoric acid and evaporate off the acids under a good hood, finally driving off the sulfuric acid by heating the crucible near the top. Heat to a dull red and weigh. The loss in weight is silica. This multiplied by 46.93 and divided by the weight of sample equals the per cent. of silicon in the sample.

The residue of tungstic acid always contains some ferric oxide and possibly some chromic oxide. To obtain these, fuse the residue with 5 grams of sodium carbonate until all tungstic anhydride is dissolved, dissolve the cold cake with hot water and filter off the residue of ferric oxide. Wash well with hot water, burn off the paper and weigh the residue. Subtract the weight so obtained from the weight of the impure tungstic oxide after the silica was driven off and the difference is the weight of the pure WO_3. Multiply this by 79.3 and divide by the weight of the sample to obtain the percentage of the tungsten in the sample.

Meanwhile, while purifying the precipitate, add to the filtrate 15 c.c. of sulfuric acid and 15 c.c. of nitric acid and evaporate until copious fumes of sulfuric acid appear to expel all the hydrochloric acid. Add 25 c.c. of nitric acid, dilute to 200 c.c. and boil until all salts are dissolved. Then add a strong solution of potassium permanganate a little at a time until a pink color persists, and then boil for 20 minutes to decompose the excess permanganate. A precipitate of manganese dioxide should remain. If it does not, not enough permanganate has been added. The solution should not be allowed to concentrate much or manganese dioxide will go into solution in a form which will titrate with ferrous sulfate.

Filter off the manganese dioxide through an asbestos mat, wash a few times with water and cool the filtrate to tap-water temperature. Dilute to 350 c.c. and titrate. Run in a N/10 ferrous sulfate solution until all yellow color of chromic (and vanadic) acid has gone and about 10 c.c. excess. Then add N/10 permanganate until a faint pink appears in the chrome green solution if much chromium is present. The pink should persist after a minute's shaking. If it does not, add more until it does. The ferrous sul-

fate used minus the permanganate used multiplied by 0.001733 (if the solutions are N/10) equals the chromium present. Or the iron value of the ferrous sulfate minus the iron value of the permanganate multiplied by 0.31 gives the chromium present.

After the chromium is titrated the vanadium may be titrated according to the method given on page 148.

Notes on the Tungsten and Chromium Determinations.—When the steel is dissolved in strong hydrochloric acid as above directed the tungstic acid does not separate until the sample is dissolved and the precipitate is not much contaminated with iron. Since a trace of tungstic acid remains in solution, also some silica, it is necessary to evaporate the filtrate to dryness to render both insoluble by dehydrating the tungstic acid and silicic acid forming the insoluble anhydrides WO_3 and SiO_2. But a fairly accurate determination of tungsten may be made by omitting the evaporation to dryness.

Tungstic anhydride is volatile if ignited at a much higher temperature than a dull red, hence the necessity for heating carefully.

There will always be a little WO_3 which adheres to the casserole and cannot be removed by a policeman. It can be removed as follows: When the casserole is well washed out and *the filter paper and precipitate thoroughly washed*, wet a piece of filter paper with NH_4OH and wipe out the casserole with it. This will remove all the tungstic acid adhering to the casserole. Add the paper to the other two papers and ignite them all together.

If the chromium in the filtrate is not desired and a tungsten determination alone is wanted, it is not necessary to evaporate the filtrate from the WO_3 to dryness. Proceed as follows: Add to the filtrate 20 c.c. of 1 : 1 hydrochloric acid solution containing 0.5 gram of cinchonine. The cinchonine precipitates the tungsten completely. Heat the solution and filter and wash with a dilute acid solution of cinchonine. Ignite the precipitate with the rest of the precipitate of WO_3.

When the filtrate from the WO_3 is evaporated to fumes of sulfuric acid the HCl is expelled. This is necessary before the chromium is determined. The sulfates will dissolve slowly, but it is not necessary to wait until they are all dissolved before adding the permanganate to oxidize the chromium to chromic acid. The reactions involved in the chromium determination are given under the determination of vanadium and chromium.

If the presence of molybdenum is suspected, the filtrate from the fusion of the WO_3 should be tested for molybdenum as directed on page 164. If molybdenum is found it should be determined.

Volumetric Method for Tungsten.—Wash the precipitate of WO_3 obtained as above directed with a hot dilute hydrochloric acid solution until the iron salts are gone, then wash with a 5 per cent. solution of KNO_3 until the washings are free from acid. It is not necessary that the WO_3 be all removed from the casserole as directed for the gravimetric method. Put the filter and contents in the casserole, run in from a burette about 60 c.c. of a N/10 sodium hydroxide solution and stir the paper about until all the WO_3 is dissolved. Then add a few drops of phenolphthalein and titrate the excess of soda with N/10 HCl until the pink color disappears. The number of cubic centimeters of soda used minus the number of cubic centimeters of acid used multiplied by 0.0092 divided by the weight of sample used and multiplied by 100 gives the percentage of tungsten.

The titration reaction is $WO_3+2NaOH=Na_2WO_4+H_2O$. If the WO_3 is very impure with iron the end point of the titration is unsatisfactory. (See J. Am. Chem. Soc., IV, 477, LINDE and TRUEBLOOD.)

REFERENCES FOR THE GRAVIMETRIC METHOD:

ARNOLD and IBBOTSON, "Steel Works Analysis," 161.
McFARLANE, "Lab. Notes on Iron and Steel Analysis," 211.
JOHNSON, "Chem. Analysis of Special Steels, Steel-making Alloys, Etc.," 59.
BLAIR, "The Chem. Analysis of Iron," 217.
McKENNA, *Proc.* Eng. Soc. Western Pa., XVI, 119.
WALTER, *Chem. Ztg.*, XXXIV, 2.
ZINBERG, *Stahl u. Eisen*, XXVIII, 1819.
BARTONEC, *Chem. Zentr.*, 1909, 2017 (gravimetric and volumetric).

Colorimetric Determination of Chromium when Present in Small Amounts.—This method devised by Garrett is particularly advantageous for use on steels containing less than 0.2 per cent. chromium. It depends upon the fact that disodium 1,8-dihydroxy-naphthalene 3,6-disulfonate is extremely sensitive to chromate solutions, giving a pink color. The method is short and accurate.

Process of Analysis.—Dissolve from 0.2 to 0.4 gram of steel (depending upon the amount of chromium present) in 10 c.c. of 1:3 sulfuric acid in a 400 c.c. flask. When solution is complete, add ½ c.c. of concentrated nitric acid and boil nearly to dryness to expel nitrous fumes and nitric acid. Do not use more nitric acid than directed. Add 50 c.c. of 10 per cent. sodium hydroxide solution and 1 gram of sodium peroxide and boil for five minutes.

There must be no peroxide left undecomposed, as it would reduce the chromate after acidification. Five minutes' boiling is sufficient. Cool the solution to room temperature and dilute to 200 c.c. in a calibrated flask. Filter off 100 c.c. and add to the filtrate 2 c.c. of 85 per cent. phosphoric acid and 8 c.c. of concentrated sulfuric. This heats the solution. Immediately add 2 c.c. of 1 per cent. aqueous solution of disodium 1,8-dihydroxynaphthalene 3,6-disulfonate. A pink to cherry-red color develops, depending upon the amount of chromium. Allow the solution to stand for 15 minutes and then compare the colors obtained from the sample and a standard steel by any convenient colorimeter.

Notes on the Process.—The standard is best made by using a chromium-free steel to the solution of which is added a desired amount of standard bichromate solution.

There is a slight retention of chromium by the iron precipitate, but since the standard is treated in the same way, this makes little error.

Vanadium interferes with the method by giving a brownish tint.

Titanium also gives a red color with the reagent, but titanium is precipitated out with the iron. The error due to the vanadium can be avoided by adding the same amount of vanadium to the standard.

Reference:

Garratt, *J. Ind. Eng. Chem.*, V, 298.

CHAPTER XII

DETERMINATION OF MOLYBDENUM IN STEEL

When an acid solution of a molybdenum steel is nearly neutralized and added to a hot sodium hydroxide solution the molybdenum stays in solution as sodium molybdate while the other metallic constituents are precipitated (except perhaps a little chromium). The sodium molybdate solution is filtered off and the molybdenum is precipitated as lead molybdate.

Process of Analysis.—Place 2 grams of the drillings in a 450 c.c. beaker and cover them with 50 c.c. of strong hydrochloric acid. Heat to the boiling-point and add, a few drops at a time, strong nitric acid. Continue to heat the solution and add nitric acid, a few drops at a time, until the sample is in solution and the iron is oxidized. Very little more nitric acid should have been added than was necessary to oxidize the iron. A black film of carbonaceous matter will remain. Now evaporate to beginning pastiness, add 50 c.c. of hot water and 10 c.c. of hydrochloric acid and boil a few minutes. The tungstic acid separates if there be any present. Filter and wash the precipitate with hot water acidulated with hydrochloric acid. To the filtrate add a solution of sodium hydroxide, shaking the flask well during the addition, until most of the free acid is neutralized, but not until a darkening in color takes place. Now transfer the solution to a separatory funnel.

Open the stop-cock of the funnel so that the solution runs out in drops and allow the drops to fall into a 500 c.c. graduated flask containing 150 c.c. of a 6 per cent. solution of sodium hydroxide heated nearly to boiling. Shake the flask vigorously while the stream of drops is running in. This is important, as otherwise some molybdenum will be carried down with the ferric hydroxide. Finally wash the funnel. The iron and all but a little of the chromium are precipitated as hydroxides. A small amount of the chromium goes into the filtrate as chromate.

Fill the 500 c.c. flask up to the mark, mix well by inverting and shaking and filter through a large paper into a 250 c.c. graduated flask, rejecting the first few cubic centimeters of filtrate. Transfer the 250 c.c. of filtrate to a 500 c.c. beaker and add hydrochloric acid until the solution just becomes acid, using methyl orange as indicator, then add 4 c.c. of hydrochloric acid, sp. gr. 1.19, in excess. Add a few drops of sulfurous acid to reduce the small amount of chromic acid usually present, and boil. Add 40 c.c. of ammonium acetate made by adding 30 per cent. acetic acid to strong NH_4OH until the NH_4OH is neutralized. Now add 40 c.c. of a 1 per cent. lead acetate solution, stir well and filter through a close filter paper and wash well with hot water. Ignite in a porcelain crucible and weigh. The lead molybdate contains 26.16 per cent. of molybdenum.

Notes on the Process.—When the sample is dissolved and oxidized with nitric acid a little molybdic acid may precipitate, and would appear with the tungstic acid if any were present.

The treatment with soda forms sodium molybdate which is soluble, while the iron separates as ferric hydroxide. If the acid solution is not added slowly and with vigorous stirring the ferric hydroxide will carry down with it some molybdic acid. The ammonium acetate is added to reduce the acidity according to the law that when a mixture of ions are present they will be so grouped that the least dissociated compound possible will be formed, in this case acetic acid instead of hydrochloric acid.

If much tungsten is present, the WO_3 should be dissolved in sodium hydroxide, diluted to 50 c.c., hydrochloric acid added until the solution is acid and 20 c.c. excess added and the solution evaporated down to 10 c.c., diluted to 50 c.c. and boiled, the WO_3 filtered off and the filtrate added to the main filtrate.

References:

Chemical News, LXXXI, 269.

Arnold and Ibbotson, "Steel Works Analysis."

McFarlane, "Lab. Notes on Iron and Steel Analysis."

Blair, "The Chem. Anal. of Iron."

Johnson, "Chem. Anal. of Special Steels, Etc."

Qualitative Test for Molybdenum.—Dissolve $\frac{1}{2}$ gram of the drillings in 25 c.c. of 1:1 HCl. Add 2 grams of $KClO_3$ and heat until the residue is bright yellow if tungsten is present. Filter and add to the filtrate 10 grams of KOH dissolved in 10 c.c. of water. Boil for several minutes. Filter and pour the solution

into a large test-tube. Add HCl until crystals of KCl begin to form, then add a few grains of granulated tin and heat just to boiling but no more. Cool and add ½ gram of KCNS. If molybdenum be present a red color develops, the depth of the color depending upon the amount of molybdenum present.

The precipitation with KOH is to separate out the iron which would also give a red color with KCNS. The solution must not be heated too long with the tin present or the delicacy of the test will be impaired. The test will indicate the presence of as little as 0.2 per cent. or less.

CHAPTER XIII

THE DETERMINATION OF TITANIUM

Titanium may be present in steels up to a few tenths per cent. It is generally present in pig-iron in small amounts. In ferrotitanium there may be as high as 75 per cent. present. Ores contain from nearly zero up to a good many per cent. of titanium.

Titanium may be determined gravimetrically by weighing as TiO_2 or volumetrically by reduction with zinc to trivalent condition followed by titration with permanganate. When present in amounts below 0.5 per cent. it is best determined colorimetrically. This is done by adding hydrogen peroxide to the 5 per cent. sulfuric acid solution and producing a yellow color which is compared with a standard solution treated in the same way. The peroxide oxidizes the titanium to the hexavalent form.

Titanium may be separated from iron when the iron is divalent by boiling the dilute slightly acid solution, when the titanium precipitates out as titanic acid. Or the titanium may be separated from the iron when to the acid solution containing the iron in the ferrous condition is added an excess of ammonia containing enough alkali cyanide to form ferrocyanide with the iron. The ferrocyanide stays in solution, while the titanium precipitates as $Ti(OH)_4$. This precipitate whether made from acid or alkaline solution, if formed from a solution containing large amount of iron, is always impure. If the precipitate is then fused with sodium carbonate and the fusion is extracted with water, the titanium remains insoluble as sodium titanate while phosphorus, silica, chromium, aluminum and vanadium go into solution. The titanate is dissolved in acid, the $Ti(OH)_4$ is again precipitated and weighed as TiO_2.

Process of Analysis (Colorimetric).—Add to 1 gram of the sample in a 500 c.c. flask 40 c.c. of 1:3 sulfuric acid. Heat to boiling until no more action takes place. Pay no attention to any residue. Dilute to 250 c.c. and add NH_4OH until a slight precipitate forms, then add a few grams of sodium thiosulfate and a few drops of sulfuric acid or enough to make the solution clear. Heat until all the iron is reduced as shown by a test of a drop with KCNS, then add a solution containing 25 c.c. of water, 15 c.c.

of NH_4OH, sp. gr. 0.9, and 10 grams of KCN. Heat to boiling for several minutes. Prepare a filter by shaking two 9-cm. filter papers in a flask until well macerated and then pouring the pulp through a funnel containing a platinum cone. Place this funnel in a suction flask and pour the solution through, using suction. The solution should filter quickly to prevent oxidation of the iron. Wash well with water.

Burn the paper and its contents in a platinum crucible until all the paper is consumed, then add 4 grams of $KHSO_4$ which has been previously fused to remove the water and fuse and maintain at a bright red heat for several minutes. Cool, then add water enough to half fill the crucible and 5 c.c. of sulfuric acid, and heat until the cake is all dissolved. Cool, transfer to a Nessler tube or other color comparitor, dilute to 100 c.c. and add 3 c.c. of hydrogen peroxide (ordinary 3 per cent. solution). If titanium is present a yellow color will immediately appear. To the other tube add 100 c.c. of 5 per cent. sulfuric acid, 3 c.c. of peroxide and standard titanium sulfate solution a little at a time, shaking after each addition, until the color matches the color in the solution of titanium from the sample. The titanium in the sample will then be the same as that added for comparison.

The above method is very accurate, only requires about 1½ hours, and vanadium does not interfere, as it would if the sample were compared directly. A Government standard sample containing 0.073 per cent. Ti gave 0.075 per cent. by the above method even when 3 per cent. of vanadium was added.

Gravimetric Method.—Fuse the precipitate obtained above with twenty times its weight of sodium carbonate and a little KNO_3 until in quiet fusion dissolve in hot water and wash with sodium carbonate solution (5 per cent). Wash at least ten times. Place the paper and residue of sodium titanate in a platinum crucible and fuse with $KHSO_4$ at a bright red until in clear fusion. Cool, dissolve in hot water containing sulfuric acid, add NH_4OH until nearly but not quite alkaline, then a gram or so of thiosulfate to reduce what little iron may be present and finally add a solution of 25 c.c. of water, 15 c.c. of NH_4OH and 1 gram of KCN. Heat to boiling and filter through a pulp filter as above directed. Wash well to remove alkali salts and if the amount of titanium is not high, ignite and weigh the TiO_2. It

should be ignited over the blast. If the sample is very high in titanium, as in a ferrotitanium, the precipitate will carry down some alkali salts and should be dissolved in sulfuric acid 1:3 and precipitated again with NH_4OH. The weight of the precipitate multiplied by 0.6005 gives the titanium.

Ores are analyzed as follows: Place 1 gram of the finely ground sample in a platinum crucible, add 10 grams of sodium carbonate and fuse until the fusion is quiet. Cool, dissolve in hot water and wash well to remove as much silica and alumina as is possible. Ignite the paper and residue in a platinum crucible, fuse with $KHSO_4$, dissolve in hot water containing 5 c.c. of sulfuric acid and proceed as with the first solution of the metal in sulfuric acid as given above, for either the colorimetric or gravimetric method.

Notes on the Process.—When a metal is dissolved in sulfuric acid it will go into solution mostly as ferrous iron, so that not much "thiosulfate" will be required. When the sample is an ore more care will be required to get all the iron reduced.

The precipitate of $Ti(OH)_4$ from an alkaline solution has no tendency to run through the filter. If the filter is a pulp one the filtration will be rapid but if a filter paper is used it will be slow.

$Ti(OH)_4$ has a strong tendency to stick to the glass, so that the precipitations should all be made in the same flask. Finally it is well to heat the flask with 5 c.c. of strong sulfuric acid until it fumes strongly and then determine the titanium thus obtained colorimetrically.

There must be no fluorine in the solution to be analyzed colorimetrically as it discharges the color of titanium with hydrogen peroxide. Also large amounts of alkali sulfates effect a slight weakening of the color.

Both chromium and aluminum precipitate from alkaline solution with titanium and should be removed upon solution of the sodium carbonate fusion when the gravimetric method is used. They do no harm in the colorimetric method. The KNO_3 is used to oxidize the chromium to chromate.

It must not be forgotten that KCN is very *poisonous* and the solution containing it must not be made acid except with the greatest care and in a good hood.

The precipitate of $Ti(OH)_4$ may contain a little nitride after ignition and be brown. If it is, it should be fused with sodium carbonate again and reprecipitated from a solution only slightly alkaline with NH_4OH.

REFERENCE:

BORNEMAN and SCHIREMEISTER, *Metallurgie*, 7, 71, 723.

Standard TiO_2 Solution.—Ignite pure TiO_2 at a dull red heat to constant weight. Weigh 0.5 gram of the anhydrous powder. Put this in a platinum crucible with 5 grams of pure potassium bisulfate. Melt cautiously and keep at a low red heat from five to ten minutes until the TiO_2 all dissolves and the liquid becomes clear. Partially cool the crucible and add 5 c.c. of concentrated H_2SO_4, then heat again till the mass liquefies. Cool, and put the crucible and contents into 200 to 300 c.c. of water containing 5 per cent. of H_2SO_4. When the fusion is dissolved, wash and remove the crucible. The TiO_2 should dissolve to a clear solution. If any residue remains, filter it out, wash and weigh it and deduct it from the TiO_2 taken, using the difference in calculating the standard of the solution. Finally dilute the solution with 5 per cent. H_2SO_4 till 1 c.c. contains 1 mg. of TiO_2. Check it by precipitating and weighing the TiO_2 from 20 c.c. This can be done by the regular gravimetric process. After weighing, the TiO_2 should be tested for SiO_2 by treating it with a little H_2SO_4 and HF, igniting and weighing the residue. Any loss will be SiO_2.

Determination of Titanium by Precipitation from Acid Solution

The following method is adapted from the method of Blair. It depends upon the fact that when a dilute, slightly acid solution of titanium is boiled the titanium is precipitated by hydrolysis, thus $Ti(SO_4)_2+4HOH=Ti(OH)_4+2H_2SO_4$. If the iron is all present as ferrous iron it does not precipitate. Aluminum if present precipitates by hydrolysis at least partially. The titanium precipitates quickly and has no tendency to run through the filter. It is apt to be impure and to require a second precipitation. Small amounts should be finally determined colorimetrically by hydrogen peroxide.

If the sample contains much phosphorus it will prevent the precipitation of the titanic acid from an acid solution. Hence the phosphorus is first removed by a sodium carbonate fusion.

Process of Analysis.—Dissolve 1 gram or more of the iron or steel in 25 c.c. of 1:1 nitric acid. When solution is complete dilute to 100 c.c. and add NH_4OH until the solution is alkaline. Boil, let settle and filter without washing. Suck the precipitate

as dry as possible, dry the paper and contents in an oven and crumble the precipitate out into a mortar. Burn the paper and add the ash to the rest of the dried precipitate. Grind the precipitate with 8 grams of sodium carbonate and a little niter and put the mixture in a platinum crucible. Fuse the mass and keep fused a half hour, cool, dissolve in hot water, filter from the insoluble ferric oxide, and wash thoroughly with hot water. Sodium silicate, sodium phosphate and sodium aluminate go in the filtrate. The titanium is left on the paper as sodium titanate with the ferric oxide. Dry this residue, transfer it to a large platinum crucible, preferably the one in which the sodium carbonate fusion was made, burn the filter, add its ash to the residue, and fuse the whole with fifteen or twenty times its weight of potassium bisulfate. In fusing with potassium bisulfate it is necessary to begin with a very low heat, and to raise the temperature very slowly and carefully to a low red heat, as the mixture has a strong tendency to boil over the top of the crucible whenever the temperature is increased too rapidly. When the lid of the crucible is raised, fumes of sulfuric anhydride should come off, and the fusion should be kept at this point for several hours, or until it is quite clear and the whole of the ferric oxide has been dissolved. Allow the fused mass to cool, add to it from 10 c.c. to 20 c.c. of strong sulfuric acid, and heat until it is perfectly liquid. When cold it will remain liquid. Pour it carefully into 400 c.c. of cold water in a 600 c.c. beaker. Add a little hydrochloric acid if necessary and 50 c.c. of strong sulfurous acid, or 5 c.c. of ammonium bisulfite. Filter into an 800 c.c. beaker, add NH_4OH until a permanent precipitate forms, redissolve with a few drops of hydrochloric acid, then test a drop with a drop of KCNS to see if all iron is reduced. If not, add a few grams of $Na_2S_2O_3$ and heat. Add a filtered solution of 20 grams of sodium acetate and one-sixth the volume of the solution of acetic acid (1.04 sp. gr.), and heat to boiling. The titanic acid is precipitated almost immediately in a flocculent condition and quite free from iron. Boil for a few minutes, allow the titanic acid to settle, filter and wash with hot water containing a little acetic acid. Dry, ignite, and weigh as TiO_2 which contains 60 per cent. titanium. Should the precipitate contain an appreciable amount of ferric oxide, fuse with bisulfate and reprecipitate. If the

amount of titanium is under 1 per cent., it is best to fuse the precipitate of TiO_2 first obtained and determine the titanium colorimetrically as described on page 167.

Ores are fused directly with sodium carbonate without previous treatment with acid, and then treated as above. The precipitate of $Ti(OH)_4$ will, however, be apt to contain aluminum hydroxide and the titanium should either be determined colorimetrically or again fused with sodium carbonate and the sodium titanate fused with bisulfate and again precipitated.

If the ore contains zirconium it will prevent the precipitation of titanium from an acid solution. It stays with the titanium after the carbonate fusion. Hence the best way is probably to precipitate both by the alkaline cyanide method and determine the titanium colorimetrically.

References:

Blair, "The Chemical Analysis of Iron," seventh edition, p. 184.
Hillebrand, *Bulletin*, U. S. G. S., p. 128.
Baskerville, *J. Soc. Chem. Ind.*, 1900, p. 419.

Bureau of Standards Method

When an iron is dissolved in hydrochloric acid of sp. gr. 1.10, all but a trace of the titanium remains undissolved. The following method is based on this fact.

Dissolve 5 grams of the sample in 40 c.c. of hydrochloric acid of 1.10 sp. gr. Filter off the insoluble matter, wash with water and ignite the residue in a platinum crucible. Add a few cubic centimeters of hydrofluoric acid and several drops of sulfuric acid and evaporate to dryness and heat to expel all the fluorine. Add several grams of $KHSO_4$ and fuse until everything is in solution, keeping the fusion at a red heat. Cool and dissolve the cake in water containing 5 c.c. of sulfuric acid. Determine the titanium in the solution colorimetrically.

CHAPTER XIV

THE DETERMINATION OF COPPER IN IRON AND STEEL

When iron is dissolved in dilute sulfuric or hydrochloric acid in the absence of oxygen the copper remains behind undissolved. Any traces of copper that dissolve are removed from solution by hydrogen sulfide.

Process of Analysis.—Dissolve 10 grams of sample in 400 c.c. of 10 per cent. sulfuric acid in a large Erlenmeyer flask. When dissolved pass in H_2S until the solution is saturated with it, filter and wash with H_2S water. Burn the paper in a porcelain crucible, cool and add to the residue in the crucible 5 c.c. of strong HNO_3 and heat until the copper oxide is all dissolved. Dilute, add 7 c.c. of NH_4OH, filter if necessary into a 100 c.c. Nessler tube and wash with water. If there is any copper present the alkaline filtrate will be blue.

To another Nessler tube add about 50 c.c. of water, 5 c.c. of nitric acid and 7 c.c. of NH_4OH. Add from a burette a standard copper nitrate solution until the color in the two tubes is exactly the same.

The dilution and temperature of the two solutions should be about the same.

If the amount of copper in the sample is too low to be easily seen in the alkaline solution, add 1 c.c. of a 1 per cent. solution of potassium ferrocyanide and then sufficient dilute sulfuric acid to make the solution slightly acid. A coppery color of copper ferrocyanide will appear if there is the slightest amount of copper present. Treat the other tube the same way and add the standard solution until the colors are the same.

Make the standard solution by dissolving 3.928 grams of $CuSO_4$, $5H_2O$ in water and diluting to 1 liter. One cubic centimeter contains 0.001 gram of copper.

Instead of determining the copper colorimetrically it may be determined in the final nitric acid solution electrolytically or by the iodine method.

CHAPTER XV

DETERMINATION OF ARSENIC IN IRON AND STEEL

This element may be estimated by dissolving 10 grams of the metal in HNO_3, sp. gr. 1.2, evaporating and baking as for phosphorus, dissolving the residue in concentrated HCl without heating, which might volatilize $AsCl_3$, diluting, reducing with Na_2SO_3 and precipitating with H_2S as As_2S_3. The As_2S_3 is then oxidized by fuming HNO_3, precipitated with magnesia mixture and weighed as $Mg_2As_2O_7$. For details, see Fresenius' Quantitative Analysis.

The following method is much shorter and is sufficiently accurate when only small percentages are present. It depends upon the volatilization of As as $AsCl_3$ when a solution containing it is boiled with HCl and a large excess of ferric and ferrous chloride. In order that the volatilization may be rapid and complete, the liquid should have its boiling-point raised to about 108°C. by the addition of $ZnCl_2$, or $CaCl_2$, and should contain concentrated HCl.

Process of Analysis.—Arrange the flask as for the evolution sulfur method. The delivery tube must have a couple of bulbs of 2 c.c. capacity in it to catch any $FeCl_3$ mechanically carried over. The test-tube receiving the vapors should stand in a large beaker of cold water.

Dissolve 100 grams of commercial $FeCl_3$ in 150 c.c. of concentrated HCl in a 500 c.c. beaker. Gentle warming accelerates the solution. When dissolved, add cautiously 4 grams of pulverized zinc. When this is dissolved, boil the solution gently for 10 minutes to expel the traces of arsenic found in the reagents. With new chemicals it is well to do this boiling in the flask, as in the regular determination, and determine the arsenic given off. If this is more than a trace, get other reagents. After boiling, cool the mixture. Weigh into the empty evolution flask 10 grams of the metal to be tested. Put 100 c.c. of cold water into the large test-tube into which the delivery tube dips. Now add the $FeCl_3$ mixture through the funnel tube, running it in very cautiously to avoid violent action. It may take 8 to 10 min-

utes to do this. Warm if necessary until the iron is dissolved; then heat to boiling and boil steadily for 15 minutes The arsenic will practically all distill over as $AsCl_3$ and condense in the water in the test-tube. The delivery tube should pass to the bottom of this tube and the water in the beaker in which the test-tube is placed be kept cold, as the liquid in the tube must not be allowed to reach the boiling-point. At the end of 15 minutes take out the test-tube and substitute a second one containing a similar amount of water, and boil the solution 10 minutes longer. The second tube should show no more than a trace of arsenic.

The liquid in the tube is poured into a beaker, and if not strongly acid is made so by adding HCl, heated to near the boiling-point and precipitated by a rapid current of H_2S. The As_2S_3 will separate promptly and may be filtered off on a small weighed filter, washed first with water, then twice with absolute alcohol, then with pure bisulfide of carbon to remove any sulfur present. Dry the precipitate at 100°C. and weigh.

The arsenic may be determined volumetrically as follows: Pour into a beaker the liquid from the tube into which the arsenic was distilled and cool it. Add a solution of sodium bicarbonate ($NaHCO_3$) until the acid is all neutralized, then add 1 c.c. of 5 per cent. solution in excess. Add starch paste and titrate with standard iodine such as is used for arsenic on page 225. The reaction is, $AsCl_3+4H_2O+2I=H_3AsO_4+2HI+3HCl$. The acid liberated is neutralized by the sodium bicarbonate present. Normal sodium carbonate or hydroxide must not be used.

Since one atom of sulfur as H_2S requires two atoms of iodine and one atom of arsenic requires two atoms of iodine, one atom of sulfur is equal to one of arsenic and the sulfur value of the iodine multiplied by $^{75}/_{32}$ gives the arsenic value of the iodine.

A black insoluble residue left when the iron is dissolved there may contain arsenic. In such a case it is best to dissolve the sample in 1:1 nitric acid, add 20 c.c. of sulfuric acid, heat to strong fumes and continue the heating until the excess of sulfuric acid is driven off. Cool, transfer the residue to a distilling flask, add the ferrous chloride solution and proceed as usual.

It is absolutely necessary to run a blank on the reagents and subtract the blank titration from the regular titration.

References:

Gibb, *J. Soc. Chem. Ind.*, 1901, p. 184.

Norris, *J. Soc. Chem. Ind.*, 1902, p. 393.

Blair, "The Chemical Analysis of Iron," p. 201.

Stead, *J. Iron and Steel Inst.*, 1895, I.

CHAPTER XVI

THE DETERMINATION OF ALUMINIUM IN IRON AND STEEL

Stead's Method.—J. Soc. Chem. Ind., 1889, p. 965. This depends upon the complete precipitation of aluminium as phosphate in the presence of sodium phosphate in boiling solutions containing an excess of sodium thiosulfate. Acetic acid and acetates do not interfere. Iron in the ferric state must be absent. Ferrous iron does not interfere. The excess of thiosulfate rapidly reduces the ferric iron at a boiling heat.

Process of Analysis.—Dissolve 11 or 22 grams of the metal, according to the percentage of aluminium in 44 or 88 c.c. of concentrated HCl. Evaporate to dryness to separate SiO_2. Take up in HCl and filter. Dilute the filtrate to 200 c.c., add 3 c.c. of a saturated solution of Na_2HPO_4, then NH_4OH till a slight permanent precipitate appears. Dissolve this by adding HCl drop by drop. Heat to boiling and add 50 c.c. of a saturated solution of sodium thiosulfate. Now boil gently till all the SO_2 is expelled, which will usually take about half an hour. Filter off the precipitate rapidly, using a larger filter, and wash it thoroughly with hot water. The precipitate consists of sulfur, aluminium phosphate and a little iron. Wash the precipitate back into the beaker. Let it settle and decant off the excess of water through the filter. To the remainder in the beaker, which should not exceed 5 or 6 c.c., add an equal volume of concentrated HCl and warm to nearly boiling, stirring it thoroughly. Now filter the solution through the same filter into a platinum dish, washing filter and precipitate thoroughly. Evaporate this solution containing the aluminium phosphate to dryness. The residue on the filter is sulfur and may be rejected. It is well to burn it, however, and examine any residue for aluminium. To the dry residue in the platinum dish add 2 grams of pure NaOH (from sodium) and 1 c.c. of water. Heat till the sodium hydrate dissolves, and then stir the residue thoroughly into it. Cool, add water and boil

five minutes. Transfer the turbid solution to a flask and dilute to 110 c.c. Filter through a dry filter and collect 100 c.c. of the filtrate, equivalent to 10 or 20 grams of the steel, according to the amount taken. Neutralize with HCl in slight excess. Add 3 c.c. of Na_2HPO_4 solution and again precipitate by adding 10 c.c. sodium thiosulfate and boiling. After the precipitate is formed and the SO_2 expelled, add 2 or 3 c.c. of a saturated solution of ammonium acetate. Boil two minutes longer and filter. Wash with hot water till free from chlorine. Burn off, ignite, and weigh as $AlPO_4$, which contains 22.18 per cent. of aluminium. Run a blank on all the reagents used and make a correction for any Al_2O_3 or SiO_2 so found. If chromium is present, it will be in part precipitated with the aluminium. Its presence will be shown by the yellow color it gives to the soda fusion. It can be removed by adding a few drops of an alkaline sulfite to this solution and boiling for some time; the CrO_3 will be reduced and precipitated. If the sample contains any titanium it will be precipitated with the aluminium and should be determined colorimetrically in the precipitate.

Ether Method

When the ether separation as given on page 155 is carried out, the aluminium passes into the aqueous solution with vanadium, manganese, nickel, etc. The aluminium can then be precipitated as above without having such a large amount of iron present.

Process.—Treat a 5 or 10 gram sample as directed on page 155 until the aqueous solution is separated from the ethereal solution. Then add 2 c.c. H_2SO_4, evaporate the solution until fumes of H_2SO_4 appear, dilute to 50 c.c. and precipitate the aluminium as directed above for the second precipitation.

See also phenylhydrazine method on page 309.

CHAPTER XVII

THE DETERMINATION OF NITROGEN IN STEEL

The presence of much nitrogen in steel is said to be very harmful to the steel. Hence the determination of it becomes of importance at times.

The following method is the one devised by Allen and perfected by Langley as it is used by the American Rolling Mills Co. It depends upon the fact that when a steel is dissolved in hydrochloric acid the nitrogen which was present as nitride is retained by the acid present as ammonium chloride. The solution is then made alkaline by sodium hydroxide and the ammonia distilled off. The distilled ammonia is then treated with Nessler's reagent with which it produces a brown precipitate of enormous coloring power, so that the minutest trace of ammonia can be recognized by the formation of a distinct yellow color. The reaction is

$$2HgK_2I_4+3KOH+NH_4OH=3H_2O+7KI+OHg_2NH_2I$$

the mercury compound being the colored precipitate.

Since the reaction is so very delicate the utmost care must be used to see that no ammonia is allowed to get into the solutions used from the air and especially prepared water and chemicals must be used. Even then it is imperative that blanks be frequently run. The determination must be made in a room in which there is no (or the least possible) quantity of free ammonia or ammonium salts in the air.

The reagents required are:

Hydrochloric Acid of 1:1 Specific Gravity, Free from Ammonia.—This may be prepared by distilling pure hydrochloric acid gas into distilled water free from ammonia. To do this, take a large flask fitted with a rubber stopper carrying a separatory funnel tube and an evolution tube. Place in the flask strong hydrochloric acid, connect the evolution tube with a wash bottle connected with a bottle containing the distilled water. Admit strong sulfuric acid free from nitrous acid to the flask through the funnel tube, apply heat as required, and distill the gas into the prepared water.

Test the acid by admitting some of it into the distilling apparatus, described further on, and distilling it from an excess of pure caustic soda, or determine the amount of ammonia in a portion of hydrochloric acid of 1 : 1 specific gravity, and use the amount found as a correction.

Solution of Caustic Soda.—Dissolve 300 grams of fused caustic soda in 500 c.c. of water, and digest it for 24 hours at 50°C. with a copper-zinc couple prepared by rolling together about 6 sq. in. each of zinc and copper foil.

Nessler Reagent.—Dissolve 35 grams of potassium iodide in a small quantity of distilled water, and add a strong solution of mercuric chloride little by little, shaking after each addition, until the red precipitate dissolves. Finally the precipitate formed will fail to dissolve: then stop the addition of the mercury salt and filter. Add to the filtrate 120 grams of caustic soda dissolved in a small amount of water, and dilute until the entire solution measures 1 liter. Add to this 5 c.c. of saturated aqueous solution of mercuric chloride, mix thoroughly, allow the precipitate formed to settle and decant or siphon off the clear liquid into a glass-stoppered bottle.

Standard Ammonia Solution.—Dissolve 0.0382 gram of ammonium chloride in 1 liter of water; 1 c.c. of this solution will equal 0.01 mg. of nitrogen.

Distilled Water free from Ammonia.—If the ordinary distilled water contains ammonia, redistill it, reject the first portions coming over, and use the subsequent portions, which will be found free from ammonia. Several glass cylinders of colorless glass of about 160 c.c. capacity are required.

The best form of distilling apparatus consists of an Erlenmeyer flask of about 1500 c.c. capacity, with a rubber stopper carrying a separatory funnel tube and an evolution tube, the latter connected with a condensing tube, around which passes a constant stream of cold water. The inside tube where it issues from the condenser should be sufficiently high to dip into one of the glass cylinders placed on the working table.

Process of Analysis.—Place 40 c.c. of the caustic soda, which has been treated with the copper-zinc couple, in the Erlenmeyer flask, add 500 c.c. of water and about 25 grams of tin-foil to prevent bumping, and distill until the distillate gives no reaction

with the Nessler reagent. While this part of the operation is in progress dissolve 3 grams of the carefully washed drillings in 30 c.c. of the prepared hydrochloric acid, using heat if necessary. Transfer the solution to the bulb of the separatory funnel tube, and when the soda solution is free from ammonia, very slowly drop the ferrous chloride solution into the boiling solution in the flask until it is all in. Heat to boiling. When about 50 c.c. of water has been collected in the cylinder, remove it and substitute another cylinder. Place 1½ c.c. of the Nessler reagent in a cylinder, dilute the distillate to 100 c.c. with the special distilled water and pour it into the cylinder containing the Nessler reagent. Take another cylinder, place therein 1½ c.c. of the Nessler reagent and 100 c.c. of the special distilled water to which 1 c.c. of the ammonium chloride solution has been added, and compare the colors of the solutions in the two cylinders. If the solution in the cylinder containing the ammonium chloride solution is lighter in color than that in the cylinder containing the distillate, place 1½ c.c. of the Nessler reagent in another cylinder, pour into it 100 c.c. of water containing 2 or more cubic centimeters of the ammonium chloride solution, and repeat this operation until the colors of the solutions in the two cylinders correspond after standing about ten minutes. When about 100 c.c. have distilled into the second cylinder, replace it and test as before. Continue the distillation until the water comes over free from ammonia, then add together the number of cubic centimeters of ammonia solution used, divide the sum by 3, and each 0.01 mg. will be equal to 0.001 per cent. of nitrogen in the steel.

CHAPTER XVIII

THE DETERMINATION OF OXYGEN IN STEEL

This important determination has not received as much attention as it should have, as the properties of steel are considerably affected by the presence of considerable amounts of oxygen. The oxygen exists in the steel as oxides of iron, manganese, silicon, titanium, aluminum, etc. The method here given depends upon the reaction between the oxide of iron and hydrogen at a high temperature with the formation of water vapor which is absorbed in phosphorus pentoxide and weighed.

Since hydrogen does not reduce the oxides of manganese, aluminum, and silicon, the oxides combined with them are not determined with this method, that is, the method determines only the occluded oxygen and the oxygen combined with the iron and other easily reduced metals. However, when the metal is a very pure iron containing only a few hundredths per cent. of manganese and a trace of silicon the result for oxygen obtained by this method must be fairly accurate. It is precisely in this kind of iron that the oxygen content must be closely watched.

The following method is the one of Ledebur as given by Cushman.[1] The writer is indebted to the American Rolling Mills Co., for the details.

A number of other methods for the determination of oxygen have been proposed, among which may be mentioned: (1) Heating the sample in a stream of dry chlorine; (2) dissolving the sample in special solvents such as copper or bromine.

In Ledebur's original method the sample is given a preliminary heating in pure nitrogen in order to burn the last traces of impurities and to get rid of all hydrocarbons. If the preliminary heating in nitrogen is dispensed with, the results will be slightly higher, but it is probable that for general work sufficiently accurate results can be obtained if the sample is carefully prepared for the combustion in hydrogen.

Samples.—The samples should consist of fine borings or shavings from a milling machine. The drillings should be taken from many parts of the ingot as FeO segregates badly. The drill or

[1] Cushman, *J. Ind. Eng. Chem.*, June, 1911.

machine tool should be scrupulously clean and free from all traces of oil or dirt, and should be geared to run slowly so as not to heat the sample while it is being cut. Lack of careful attention to this point will lead to high results owing to surface oxidation of the fine particles of the drillings. The drillings should be dried in a desiccator.

Apparatus.—The apparatus used in making the oxygen determination is shown in Fig. 11.

A 4 liter Kipp generator is used for generating the hydrogen. It should be charged with drillings of pure iron or mossy zinc, and dilute hydrochloric acid (1:1). Steel turnings should not be used in the generator, as the object is to generate the purest

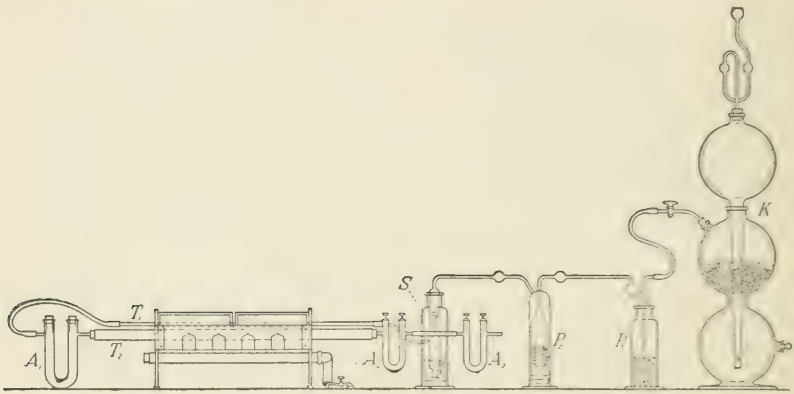

Fig. 11.

possible hydrogen. Hydrochloric is preferable to sulfuric acid. After its formation the hydrogen is purified and dried by passing through the usual train as shown in the figure. It passes first over stick potash, and next through a 30 per cent. potash solution. This solution in the second bottle should be renewed as soon as it shows a tinge of yellow due to the presence of sulfides. The hydrogen next passes through concentrated sulfuric acid to dry it, and then enters a silica tube with $\frac{1}{4}$ in. bore, 30 in. in length, which contains a roll of platinum gauze or palladiumized asbestos. The $\frac{1}{4}$ in. tube lies on top of a 1 in. $\times$ 30 in. fused silica tube contained in a suitable 12-in. gas blast furnace. It is better to preheat the hydrogen in a separate furnace.

The object of the preliminary heating over platinum foil is to free the hydrogen from the small quantity of oxygen which it always contains. If this precaution is not taken, the results will be too high. The water formed in the small-bore tube is caught in a U-tube shown in the figure, which contains phosphoric anhydride opened up with glass wool. This drying tube has rubber stoppers. The connection is made with pure gum tubing and is permanent, the sample being introduced from the opposite end of the combustion tube. All rubber connections should be made tight as directed on page 277.

Blanks should be run from time to time to make sure that the apparatus is in good order and everything working properly. Samples should not be introduced into or removed from the combustion tube when it is more than hand hot, but silica tubes may be quickly cooled with perfect safety by turning off the gas and allowing the cold air blast to play on the tube.

Process of Analysis.—Weigh 20 to 30 grams of finely divided borings into a nickel boat ½ in. × 1½ in. × 6 in. The boat with its charge is quickly inserted into the combustion tube at the right end and pushed to the middle zone by means of a rod of suitable length. The stream of hydrogen should be passing freely when the tube is opened for the insertion of the sample. After the stopper is replaced, the weighing tube and guard tube are finally connected up with pure gum tubing. The weighing tube is a 4 in. U-tube, with ground glass stoppers, containing phosphoric anhydride opened up with glass wool. The guard or trap tube is similarly charged and is intended to prevent the drawing back of moisture from the air of the laboratory. After the apparatus is all connected and in good order, the pure dry hydrogen should be allowed to sweep through a few minutes until all air is removed from the entire system. The gas is then lighted, the blast turned on and the temperature run up to a bright red heat, about 850°C. This heat is maintained for 30 minutes while the hydrogen is passing through the apparatus at the brisk rate of about 100 c.c. per minute. After the combustion is completed the gas is turned off the furnace, leaving the blast playing upon the hot tube. The stream of hydrogen should continue to pass until the tube is cool enough to bear the hand upon it.

Immediately after the tube is cool enough, the weighing tube, with its guard tube, is disconnected and connected with a suitable aspirator, so as to suck out the hydrogen gas and replace it with air dried over P_2O_5. A suitable aspirator consists of a 4 liter aspirator bottle filled with water. The upper tubular of the bottle is guarded with a calcium chloride tube to which the weighing tube is connected. A gas washing bottle containing concentrated sulfuric acid follows the phosphoric anhydride tube which is connected to the other side of the weighing tube.

Notes on the Process.—The aspirator may be roughly calibrated by allowing about 500 c.c. of water to run out of the lower tubular of the aspirator. A sufficient quantity of perfectly dry air is drawn through to thoroughly displace all the hydrogen. After all is ready, the weighed tube is closed by its glass stop-cocks, disconnected from its guard tube and placed in a desiccator for 15 minutes before being weighed. Eight-ninths of the increased weight of the tube is oxygen. The blanks on the apparatus establish the average correction to be subtracted from the weight found. The correction on an apparatus in good order should not exceed 2 mg. On damp days the blank is usually a little higher than when the air is dry.

If the stop-cocks on the weighing tube are ground so as to fit very tightly it is not necessary to displace the hydrogen with air. If the cocks do not fit very tightly some hydrogen will diffuse out.

In charging the weighing tube with phosphoric anhydride and glass wool, take care to remove any specks of phosphoric anhydride from the upper portions of the tube.

The following points should be given careful attention in order to attain the highest degree of accuracy:

Samples must be clean, absolutely dry and free from oil. They should be cut, preferably with a milling machine tool running at a low rate of speed. The samples must not heat in cutting. Sheet samples are first cleaned from oxide on an emery wheel, avoiding heating as much as possible. The sheet should be milled on the edge.

Whenever possible, samples should be cut from bars which are first cleaned by a superficial cut with the milling tool. Extreme care must be taken in the preparation of the sample.

The entire apparatus must be kept to the top notch of cleanliness, tightness and general good order. Blanks should be run frequently. Analyses should be in duplicate whenever the results are to be used as a basis for specification. The most extreme care should be taken to exclude all oxygen from the sample and apparatus except that which

it is the object of the method to determine. When determining oxygen in pure iron, the silver white iron residues from the boat may be reserved for charging the Kipp hydrogen generator.

Method for Total Oxygen

This method depends upon the reduction of the oxides by carbon in a vacuum furnace at a very high temperature. The carbon monoxide formed is passed through iodine pentoxide forming carbon dioxide and liberating iodine which is absorbed in potassium iodide and titrated with sodium thiosulfate. (See Walker and Patrick, J. Ind. Eng. Chem., Nov., 1912, p. 799.)

CHAPTER XIX

DETERMINATION OF HYDROGEN IN STEEL

The following method is the one used by the American Rolling Mills Co.

Some of the hydrogen is liberated by drilling, so that it is necessary to work with the metal in a single piece, if possible. However, if the metal is in strips, several can be used for an analysis.

The method is based on the fact that hydrogen is liberated by heating the metal to a red heat in an atmosphere of oxygen. The hydrogen is oxidized to water, which is absorbed in phosphoric anhydride.

The apparatus used (Fig. 12) consists of a 12-in. gas blast furnace in which is placed a 30 in. $\times \frac{3}{4}$ in. silica tube, and on

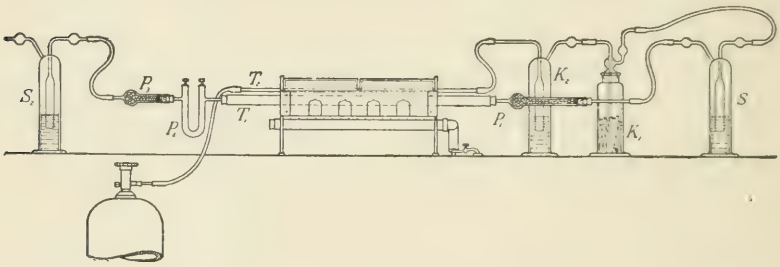

Fig. 12.

top of this tube is placed a 30 in. $\times \frac{1}{4}$ in. silica tube. The silica tubes each have a 6 in. roll of platinum gauze or palladiumized asbestos to act as a catalyzer. The oxygen gas passes through the $\frac{1}{4}$ in. silica tube (T–2) at the rate of 100 c.c. per minute, and the impurities are thus oxidized. The gas then passes through a wash bottle containing a strong solution of caustic potash (K–2), then through a bottle containing stick caustic potash (K), then through a bottle containing concentrated sulfuric acid (S–1), and finally through a tube containing phosphoric anhydride opened up with glass wool (P–1). The purified oxygen then enters the $\frac{3}{4}$ in. silica tube (T–1), where

it combines with the liberated hydrogen, forming water, which is swept into the 4 in. glass stop-cock U-tube containing phosphoric anhydride opened up with glass wool (P–2). This tube is weighed and connected with a tube of phosphoric anhydride opened up with glass wool (P–3) used as a trap. The gas finally passes through a solution of concentrated sulfuric acid, which is used to show that the gas is passing through the apparatus.

Process of Analysis.—The silica tubes should be at a red heat and oxygen should pass through the apparatus at the rate of 100 c.c. per minute. Place the sample in either a clay boat, or one of platinum containing ignited alundum, in as large pieces as are available, using from 10 to 40 grams for a determination.

Weigh U-tube (P–2) and connect direct with stopper to ¾ in. silica tube. Remove stopper and tube (P–1) and insert the boat into the red-hot zone of the silica tube. Connect tube (P–1) with silica tube and continue passing the oxygen gas through the apparatus at the rate of 100 c.c. per minute for 30 minutes. At the end of this time disconnect weighing tube (P–2) and connect with a suitable aspirator, so as to suck out the oxygen and replace it with dry air. A suitable aspirator consists of a 4 liter aspirator bottle filled with water. The upper tubular is guarded with a calcium chloride tube to which the weighing tubes are connected, and the other side of weighing tube is connected with a phosphoric anhydride tube followed by a washing bottle containing concentrated sulfuric acid.

The aspirator may be roughly calibrated by allowing 500 c.c. of water to run out of the lower tubular of the aspirator. This is a sufficient amount of dry air to thoroughly displace all the oxygen.

The glass stop-cocks of the weighing tube are now closed and weighing tube disconnected from the guard tube and placed in a desiccator for 15 minutes before being weighed. One-ninth of the increased weight of the tube is hydrogen.

Notes on the Process.—It is absolutely necessary to run a blank determination using the same amount of oxygen as for a regular test, and it must also be run for the same length of time. The blank should never exceed 1 mg. This blank is derived from the oxidation of the rubber

connections, hence the necessity for using a definite amount of oxygen for a definite length of time.

In charging the weighing tube with phosphoric anhydride, take about a gram on glass wool, fold the glass wool over the phosphoric acid and insert into the tube. Repeat until the tube is full. Use great care to remove all specks of phosphoric anhydride from the inlet and exit tubes of weighing tube.

The temperature of the silica tubes must be regulated so that the sample does not absorb all the oxygen. If the temperature is too high this will occur and no oxygen will pass through the apparatus.

It is not necessary to burn all the metal to oxide; the time that would be required to do so would be prohibitive on large samples.

CHAPTER XX

THE DETERMINATION OF SPELTER AND TIN PLATE COATING

The basis of this test is as follows:

When a zinc-coated iron article is placed in lead acetate solution at ordinary temperatures, the zinc passes into solution, and an equivalent amount of metallic lead is precipitated in a loosely adherent form upon the specimen. The reaction is retarded by the precipitation of the lead, and, therefore, when a heavily galvanized piece is being tested, this lead must be periodically removed. Should lead plate on, it is not easily confounded with the bright iron when exposed. The uncovering of the iron can be readily detected.

The solution used for making this test is prepared by dissolving 400 grams of crystallized lead acetate in 1 liter of water. When dissolved, add 4 grams of finely powdered litharge, and agitate until most of it has dissolved. The solution is allowed to settle and the clear portion decanted for use.

Ordinary glass tumblers have been found very satisfactory to use in making this test, as they are the right diameter to enable the sample to be maintained in an upright position without supports.

The samples should be taken from various parts of the sheet. Use several 2 in.$\times$2 in. pieces cut accurately. Weigh the samples together and submerge separately, for three minutes, in tumblers containing solution of lead acetate. The samples are then taken out and the adherent lead removed with a stiff brush or steel spatula. A burnishing action should be avoided, as under some conditions closely adherent lead will be plated out on the iron. Repeat the three-minute immersions in the lead acetate solutions until a bright surface is exposed. Four three-minute immersions are usually sufficient. Wash specimens in water, dry and weigh. The loss in grams represents the coating, which, divided by the number of 2 in.$\times$2 in. pieces used and

multiplied by 1.27 gives the number of ounces of coating per square foot, counting the zinc as from one side.

Analysis of Tin and Terne Plate and Lead-coated Sheets. Method of the American Rolling Mills Co.

Several samples exactly 2 in.×2 in. should be taken for analysis. Clean thoroughly with carbon tetrachloride or gasoline and weigh. A 400 c.c. Jena glass beaker has been found the most convenient for this test. We have found that 20 c.c. of concentrated sulfuric acid is sufficient for each 2 in.×2 in. piece. If four pieces are taken, however, 60 c.c. of sulfuric acid will be sufficient. Place the requisite amount of acid in the beaker and heat to at least 250°C. Wrap a stiff platinum or nickel wire around one of the 2 in.×2 in. pieces so that it can be placed in the acid in a horizontal position. Immerse the piece in the hot acid for exactly one minute. Transfer the piece to another 400 c.c. beaker containing 25 c.c. of distilled water and rub the surface of the sample while washing with about 50 c.c. more distilled water, using a wash bottle for this purpose. Dry the sample thoroughly and reweigh. The loss in weight represents the coating and some iron. Repeat this operation for each sample, collecting all rinsings in a beaker, and reserve for analysis.

The iron which has dissolved is determined as follows: The sulfuric acid is carefully poured into the beaker containing the washings from the 2 in.×2 in. pieces. This solution is cooled and poured into a volumetric flask. Twenty-five per cent. by volume of concentrated hydrochloric acid is added and the flask filled to the mark with distilled water. If four pieces have been taken for analysis, a 500 c.c. volumetric flask will be required. Use a proportionately smaller flask if less than four samples are analyzed. Mix thoroughly, and transfer 100 c.c. of the solution to a 300 c.c. Erlenmeyer flask. Add a solution of tenth-normal permanganate until iron and tin are oxidized, which is indicated by the appearance of a permanent straw color. No account is taken of the amount of permanganate used. Heat to boiling and reduce carefully with stannous chloride. Cool and pour into a 1000 c.c. beaker containing 500 c.c. of distilled water and 25 c.c. of saturated solution of mercuric chloride, stir vigorously,

add 50 c.c. of the titrating mixture of phosphoric acid and manganese sulfate, and titrate with tenth-normal permanganate to pink color. The amount of iron which has thus been determined is subtracted from the total weight lost in sulfuric acid; the remainder is coating. It is very often unnecessary to make an analysis of the coating, the object being merely to determine the weight.

There are several ways of expressing the weight of the coating; we prefer to express it in ounces per square foot. By knowing the number of square feet in a box of tin plate or a case of terne plate there is no confusion in converting the ounces per square foot to pounds per box or case. The coating on tin plate is sometimes expressed in pounds per box of 112 sheets 14 in. $\times$ 20 in. This figure can be obtained by multiplying the number of grams of coating of each 2 in. $\times$ 2 in. piece by 17.29. If it is desired to express the coating on terne plate in pounds per case of 112 sheets 20 in. $\times$ 28 in., then multiply the number of grams of coating on each 2 in. $\times$ 2 in. piece by 34.57. The average of the several pieces represents the weight of coating.

If the determination of tin and lead is desired in the sheet, proceed as follows: Place another 100 c.c. of the sulfuric acid solution containing the coating in a 300 c.c. Erlenmeyer flask. Whether lead sulfate is or is not removed with this 100 c.c., does not influence the accuracy of the tin analysis. Add 50 c.c. of concentrated hydrochloric acid and 1 gram of finely ground antimony. Connect flask with a one-hole stopper containing a glass tube bent twice at right angles, the end of which projects into a beaker of water. Boil five minutes and replace the beaker containing the water with one containing an 8 per cent. solution of bicarbonate of soda prepared from boiled distilled water. Remove flask from hot plate and allow the soda water to flow back into the flask while cooling same with tap water. When cold, add a few cubic centimeters of starch solution and titrate to permanent blue color with tenth-normal iodine solution. One cubic centimeter equals 0.00595 gram of tin. The amount of tin found is subtracted from the weight of coating which has been determined by loss in sulfuric acid, and after the iron correction has been made the remainder is lead.

An example of a regular analysis of terne plate is as follows:

Piece 2 in. × 2 in. weight	7.563 grams
Same after stripping in acid weighs	6.721 grams
Loss, coating plus iron weighs	0.842 grams

Sulfuric acid and washings were diluted to 200 c.c., 100 c.c. of which was titrated for iron. This required 10.1 c.c. of tenth-normal permanganate, which is equivalent to 0.0564 gram of iron. As half of the solution only was taken for analysis, it is necessary to multiply by 2, which is equivalent to 0.1128 gram iron.

Total weight of coating plus iron	0.8420 gram
Weight of iron dissolved	0.1128 gram
Coating	0.7292 gram

$0.7292 \times 34.57 = 25.21$ lb. coating per case of 112 sheets 20 in. × 28 in.

The tin was then determined in 50 c.c. of the sulfuric acid solution. This required 7.8 c.c. of tenth-normal iodine.

$$7.8 \times 0.00595 \times 4 = 0.1856 \text{ gram tin}$$

Coating	Tin	Lead
Grams 0.7292	= 0.1856	= 0.5436

By knowing the original weight of coating and the weight of tin and lead in this coating, it is a very simple matter to determine the percentage of each element.

In the determination of tin in tin plate it is only necessary to determine the loss in sulfuric acid, and then to determine the iron which has been dissolved, the remainder being tin.

Heavily coated lead sheets may require twice as much acid and a temperature of 300°C. to completely remove the coating in one minute.

CHAPTER XXI

THE DETERMINATION OF ZINC IN ORES

Zinc usually occurs in ores as sulfide, oxide, carbonate or hydrosilicate. All of these minerals are decomposed by boiling in the proper mineral acids. Ores containing zinc spinel (Gahnite) cannot be decomposed by acids and must be fused before treatment with acids. Oxidized ores should be first treated with HCl before nitric acid is used.

Solutions of zinc in hydrochloric acid are completely precipitated by potassium ferrocyanide. Many other metals are also precipitated by this reagent including iron, copper, manganese, and cadmium, and if these are present in the ore, they must be removed before the zinc is titrated.

The hydrochloric acid solution of zinc which is to be titrated must not contain free chlorine, bromine or oxides of chlorine, as these decompose the ferrocyanide and produce a green-colored precipitate, making results run high. Zinc ferrocyanide is white. The following method is the process of von Schulz and Low modified.[1]

Process of Analysis.—Place 1 gram of the ore in a 250 c.c. beaker, add 5 c.c. of concentrated HCl, heat for several minutes, add 20 c.c. of HNO_3 and boil with the cover on, until all brown fumes are expelled. Remove the beaker from the heat, add 1 gram of $KClO_3$ and boil to dryness. A blast of air over the solution greatly expedites the evaporation. Do not bake the residue. Now add 50 c.c. of hot water and ½ gram of KOH; but *not more* than this amount of KOH. Break up the cake on the bottom of the beaker with a policeman, then add 7 grams of $(NH_4)_2CO_3$ and heat nearly to boiling for several minutes. Let the precipitate settle, filter, preferably by suction, and wash several times with a hot 5 per cent. $(NH_4)_2CO_3$ solution. Wash the precipitate back into the beaker with a jet of water from the wash bottle. Dissolve with 4 c.c. of HCl and a little KNO_2 to reduce the MnO_2 which may be present, using heat to hasten the solution. Now add strong KOH solution until all free acid is neutralized and

[1] Low, "Technical Methods of Ore Analysis," Demorest, *J. Am. Chem. Soc.*, V, 302.

the iron precipitates, but do not add an excess of KOH. Then add 5 grams of $(NH_4)_2CO_3$, heat to boiling and filter through the same paper that was used before. Wash several times with hot ammonium carbonate solution.

Make the filtrate, which should amount to about 200 c.c., acid with HCl, keeping the cover on to prevent loss due to effervescence. Then add 20 c.c. more of HCl, sp. gr. 1.2, heat to 70°, pass H_2S through the solution for several minutes, and when the copper is practically all precipitated, gradually and with stirring add 10 c.c. of NH_4OH, sp. gr. 0.9, and continue to pass the H_2S for several minutes. Again heat to 70° and titrate with ferrocyanide. The volume at the beginning of the titration should be about 250 c.c. Fifty cubic centimeters of this may be reserved until the other four-fifths is titrated, then the 50 c.c. is added and, knowing the approximate end point, the titration can be finished without consuming much time. The titration must be performed slowly and with constant stirring to get the best results.

Standardization of the Ferrocyanide.—Dissolve 22 grams of pure $K_4Fe(CN)_6 \cdot 3H_2O$ in water and dilute to 1 liter. One cubic centimeter of this solution will precipitate approximately 0.005 gram of zinc.

Weigh 0.2 gram of pure zinc, or better, the amount of zinc which is approximately that which the sample is supposed to contain. Dissolve in 10 c.c. of HCl and 20 c.c. of H_2O, add 10 grams of NH_4Cl, dilute to 250 c.c., heat to 70° and titrate. Run in the ferrocyanide slowly and with constant stirring until a drop of the solution shows a brown tinge when tested on a white plate with a drop of a 5 per cent. solution of uranyl nitrate after standing a minute.

A blank must be run, using the same amount of reagents and solution as in the standardization. This generally takes about 0.3 c.c. of the above solution and this amount must be subtracted from the amount of ferrocyanide used in the standardization and in the titration of the ore. It is necessary that standardization be made under the same conditions of temperature, volume, and acidity as obtain when the ore is titrated.

Notes on the Process.—Manganese is precipitated at the first from the acid solution as MnO_2 by means of potassium chlorate because when

it is precipitated from an alkaline solution as MnO_2 it carries down zinc as zinc manganate.

Potassium hydroxide is used to combine with any NO_3 ions present in order to prevent the formation of ammonium nitrate upon the addition of ammonium carbonate, because cadmium carbonate is soluble if much ammonium salt other than the carbonate is present.

The ammonium carbonate precipitates the lead, cadmium and any manganese in solution as carbonates, the iron and aluminum precipitate as hydroxides and, of course, any lime or magnesia present comes down as carbonate. The zinc and copper dissolve as zinc and copper ammonia carbonates. If the amounts of the elements which precipitate are small one separation is enough but it is always best to make the double separation and not much additional time is consumed.

When the copper is precipitated according to the above directions, that is, by hydrogen sulfide from a very acid solution, the copper comes down free from zinc. What little copper remains in solution is precipitated as the solution is gradually made less acid. The copper sulfide need not be filtered off, as it does not interfere with the titration even when the copper is present in amounts as high as 20 per cent. of the sample, for it precipitates in a very dense form.

The potassium chlorate used in the decomposition of the ore introduces no complications unless used in abnormally large amounts for it is reduced by the action of the hydrogen sulfide and the presence of the hydrogen sulfide during titration prevents any oxidation of the ferrocyanide.

The use of lead or aluminium to precipitate the copper and cadmium is inadvisable as they tend to make results erratic. Lead is least harmful.

The titration for standardization should be made under the same conditions as to temperature, acidity, volume, amount of ammonium salt, and rate of titration as obtains when the ore is titrated. The amount of free acid should not be greater than about 5 per cent. of HCl, sp. gr. 1.2.

It is absolutely necessary that the titration should not be made too rapidly. If the ferrocyanide be run in rapidly and without much stirring, the end point will seem to be reached long before the zinc is all precipitated. If, however, the solution be then allowed to stand for several minutes while being vigorously stirred, the titration may be finished without error. Probably when the ferrocyanide is added rapidly, zinc potassium ferrocyanide is precipitated which can react with uranyl nitrate giving a brown color.

If zinc spinel is in the ore, the method must be modified as follows: The ore is dissolved as above. The gangue left on the filter paper should

be ignited and fused with the sodium carbonate mixed with a little borax glass, until decomposition is complete. The melt is dissolved in HCl and added to the main solution, and the analysis carried on as usual.

None of the constituents of zinc ores interferes with the above process. Nickel if present would count as zinc. The writer has tested the method on the Government standard ore which contains 31.4 per cent. zinc. He put in 10 per cent. each of manganese, iron, copper, lead and cadmium without causing more than $\frac{1}{10}$ to $\frac{3}{10}$ per cent. error.

Method of Von Schultz and Low.—Weigh 1 gram into a 4 in. casserole. Add 2 or 3 c.c. of concentrated HNO_3, then cautiously 25 c.c. of HNO_3, previously saturated with $KClO_3$ by shaking up with crystals of the salt. (Keep this solution in an open bottle.) When the violent action is over, cover the casserole and boil rapidly to dryness. Do not bake the residue. Now cool and add 7 grams of NH_4Cl, 25 c.c. of hot water and 15 c.c. of strong NH_4OH. Boil the liquid one minute, add bromine water and then rub the dish with a rubber-tipped rod to loosen and disintegrate all the insoluble matter. Filter and wash several times with a boiling-hot 1 per cent. solution of NH_4Cl. If the filtrate is *blue* copper is present.

Add to the filtrate 25 c.c. of concentrated HCl and dilute to 200 c.c. If copper is present add 40 grams of "granulated lead" and stir until the liquid is colorless. Titrate the hot solution as above described.

For a complete bibliography of zinc analysis see The Journal of Industrial and Engineering Chemistry, IV, p. 468.

The Modified Waring Method for Zinc (J. Am. Chem. Soc., XXIX, 265).—This method is accurate and especially valuable when there are large amounts of manganese present. It depends upon the separation of lead, copper and cadmium from zinc by means of metallic aluminium, and zinc from iron, aluminium and manganese by means of hydrogen sulfide in a solution very slightly acidified with formic acid.

Calamine, willimite, franklinite, blende, smithsonite and other soluble minerals are decomposed by aqua regia, with subsequent evaporation with sulfuric acid to remove nitrous compounds. If zinc spinel (Gahnite) is present the insoluble residue must be fused with sodium carbonate and borax glass, the fusion dissolved and the solution added to the main solution. If much silica is present the borax glass may be dispensed with. Silicates such as cinders from oxide furnaces and some slags and natural

silicates must be fused with sodium carbonate before solution with hydrochloric acid.

Process of Analysis (For soluble ores).—Treat 0.5 gram to 1 gram of the ore in an Erlenmeyer flask with 10 c.c. of hydrochloric acid until the residue is white, then add 5 c.c. of nitric acid and 5 c.c. of concentrated sulfuric acid and digest until the ore is completely decomposed. Then evaporate to copious fumes of H_2SO_4 to expel all nitric and hydrochloric acids. Dissolve the mass in 50 c.c. of water and add enough sulfuric acid to bring the amount of free acid up to 10 per cent. Introduce a piece of sheet aluminium which is too large to lie flat on the bottom of the beaker and boil to complete reduction (about 10 minutes). Filter and wash through a filter containing pieces of aluminium to keep the iron reduced. The receiving beaker should contain a stirring rod of aluminium. Cool the solution, add a drop of methyl orange, and neutralize with *sodium bicarbonate* to a light straw color. Add drop by drop 20 per cent. formic acid until the pink color is just restored, then 5 drops more. (Dilute hydrochloric, 1 :6, may be substituted for formic acid when ammonium thiocyanate is to be introduced.) Dilute to about 100 c.c. for each 0.1 gram of zinc present; if much iron is present add 2 to 4 grams of ammonium thiocyanate, remove the strip of aluminium, heat nearly to boiling, and saturate with hydrogen sulfide. Allow the pure white ZnS to settle a few minutes, then filter and wash with hot water. Transfer the precipitate and filter to a large beaker, dissolve with 10 c.c. of hydrochloric acid and 40 c.c. of water, using heat, until all zinc is in solution. Determine the zinc as pyrophosphate containing 42.89 per cent. of zinc, or by titration with ferrocyanide.

To determine the zinc as pyrophosphate, filter the solution of the ZnS in hydrochloric acid and make the filtrate cold, dilute and slightly acid. Then add a *large* excess of ammonium sodium hydrogen phosphate and neutralize very carefully with NH_4OH, adding it drop by drop, finally adding a drop or two in excess. Finally add about 1 c.c. of acetic acid and warm gently until the flocculent precipitate of $ZnNH_4PO_4.H_2O$ has settled as a dense crystalline powder. Filter and wash with hot water.

Dry the precipitate, separate the paper from it and burn the paper. Add the ash to the precipitate and ignite the two, gently at first, then for a few minutes at a bright red heat. Cool and weigh as $Zn_2P_2O_7$ containing 42.89 per cent. of zinc.

Instead of determining the zinc gravimetrically it may be finally titrated with ferrocyanide under the same conditions as previously given.

Notes on the Process.—Any copper which the aluminium does not precipitate will come down with the zinc but will not dissolve with the latter in hydrochloric acid.

In neutralizing, if the solution is strongly acid, it is better to nearly neutralize with sodium hydroxide and then finish with bicarbonate. This saves time and prevents loss by foaming.

It is not necessary to pass the hydrogen sulfide under pressure if the diluting is done as directed. The gas should be passed through until a drop of the solution blackens a drop of alkaline nickel sulfate. It is necessary that the solution be quite hot during the precipitation of the sulfide. If the heating has taken much time the formic acid may have volatilized and more must be added.

The flocculent $ZnNH_4PO_4.H_2O$ is very soluble in the mineral acids as well as in ammonia, but after crystallization it is much less soluble in the latter. It is only slightly soluble in acetic acid; an excess of 1 c.c. in 100 c.c. of solution does not dissolve an appreciable amount. It is somewhat soluble in all ammonium salts unless considerable excess of phosphate is present.

CHAPTER XXII

THE DETERMINATION OF COPPER IN ORES

Most copper ores are soluble in strong mineral acids. In dissolving an ore it is best to treat first with hydrochloric acid to dissolve oxidized minerals, then with nitric acid to dissolve sulfide minerals. Slags may require fusion with Na_2CO_3 or treatment with HF.

There are in general use four methods for the determination of copper in ores. They are the iodide, electrolytic, cyanide and thiocyanate methods. The electrolytic method is the most accurate for use on ores which do not contain arsenic, antimony or bismuth, but for analyzing these impure ores or miscellaneous ores whose nature is not known, the iodide method is the most applicable because it is accurate and rapid, and the above elements do not interfere.

The Iodide Method for Copper

This method depends upon the fact that in a solution slightly acid with acetic acid cupric compounds oxidize potassium iodide with the liberation of iodine. This is then titrated with a standard thiosulfate solution. The reactions are:

$$Cu(NO_3)_2+2KI=CuI+2KNO_3+I$$

and,

$$2I+2Na_2S_2O_3=2NaI+Na_2S_4O_6.$$

The copper iodide is precipitated as a white precipitate. The titration is accurate and the end point sharp. Of course there must not be anything present, besides copper, which will liberate or absorb iodine. Nitrous oxides, ferric ions, free bromine, trivalent arsenic and trivalent antimony must be absent as they will either absorb or liberate iodine. Excess of free mineral acids must not be present. Pentavalent arsenic and antimony do no harm. Bismuth and lead if present in solution cause some trouble by making it difficult to see the end point owing to the formation of yellow iodides, but otherwise cause no trouble. The following method can be much shortened by using the modification on page 202.

Process for Ores.—Take enough of the finely ground ore for a sample so that there will be present from 0.05 gram to 0.40 gram

of copper. Put in a 250 c.c. beaker and add 7 c.c. of concentrated HCl and heat. Then add 10 c.c. of strong HNO_3 and heat until the ore is completely decomposed. Then add 7 c.c. of strong H_2SO_4 and evaporate until the sulfuric acid fumes strongly. Cool and add 30 c.c. of water and heat until all soluble salts are dissolved. Cool, add 4 grams of granulated zinc and shake for several minutes. The copper will be quickly precipitated. Heat until the zinc is dissolved, then add 25 c.c. of H_2S water to make sure that the last traces of copper are precipitated. Filter and wash several times to remove all iron salts. Wash the precipitated copper back into the beaker with a jet of water, using not more than 10 c.c. of water if possible, in order to avoid having a dilute nitric acid solution. Add 7 c.c. of strong HNO_3, heat until all copper goes into solution, and boil until nitrous fumes are expelled. Then pour the hot solution through the filter paper, wash the paper with 5 c.c. of bromine water to dissolve any copper sulfide there. Finally wash the beaker and paper thoroughly with water. The bromine also oxidizes any nitrous oxide and arsenic or antimony present.

Heat the filtrate to boiling and boil vigorously for not less than 10 minutes to expel all bromine. Cool and add ammonia or sodium hydroxide until the solution turns blue or becomes just alkaline. Do not add an excess of alkali. If an excess is added, drop in a few drops of sulfuric acid until the excess is neutralized, then add alkali again. Now add acetic acid until the liquid becomes acid, then add 2 or 3 c.c. of 80 per cent. acetic acid in excess. Cool to tap-water temperature.

Dissolve 3 grams of KI in a few cubic centimeters of water, add it to the solution to be titrated and stir well. It immediately becomes brown due to the liberated iodine. From a burette run the standard thiosulfate solution in until the brown color is nearly gone, then add 5 c.c. of starch solution. Continue the addition of the thiosulfate carefully until one drop turns the solution from a blue to a white or yellowish-white. This is the end point. It should be stable and the blue color should not reappear upon standing five minutes. If the blue reappears it indicates faulty work. If the solution is not sufficiently acid the end will not be sharp.

Standardization of the Thiosulfate.—Dissolve 19.55 grams of pure $Na_2S_2O_3.5H_2O$ in water, add 1 gram of NaOH and dilute to 1 liter. The water should be free from CO_2, and the solution should be kept in the dark. Also make a starch solution as directed on page 100.

Weigh carefully about 0.2 gram of pure copper wire or foil. Place in a 250 c.c. beaker and dissolve in 10 c.c. of 1 :1 HNO_3. Dilute to 25 c.c., boil off the red fumes, then add 5 c.c. of bromine water and boil about 10 minutes or until the bromine is all expelled. Remove from the heat, dilute to 75 c.c., add NH_4OH until the solution becomes just alkaline (becomes blue) but not more. Add acetic acid until the solution becomes acid, then 2 c.c. more of strong acetic acid. Cool to tap-water temperature, add 3 grams of KI dissolved in 15 c.c. of water and stir a moment. Now run in the thiosulfate solution from a burette until the yellow color of free iodine has nearly gone and then add 5 c.c. of starch solution. This should produce a marked blue color. Continue the titration cautiously until on the addition of another drop the blue color of starch iodide disappears. There should be no difficulty in locating the end point within a single drop. One cubic centimeter of the thiosulfate solution should be equal to 0.005 gram copper.

Notes on the Process.—Aluminium may be used in place of zinc to precipitate the copper but zinc acts more rapidly and certainly. It is possible to precipitate all the copper with the zinc but is best to add the hydrogen sulfide always, to make sure of complete precipitation. Of course arsenic, antimony, silver, bismuth, etc., also precipitate. Lead remains insoluble as lead sulfate.

The addition of bromine water is absolutely necessary in analyzing ores containing arsenic or antimony in order to oxidize them to the pentavalent state. If they are not so oxidized, the iodine liberated by the copper will be used up in oxidizing arsenic and antimony from trivalent to pentavalent condition. The bromine also insures complete solution of the copper sulfide and absence of nitrous oxides. Excess bromine must, of course, be boiled off.

It is necessary to use a large excess of KI to hold the liberated iodine in solution and make the reaction rapid.

Lead and bismuth having yellow iodides cause trouble if present by making it very difficult to tell when to add the starch, but with experience this is not a serious trouble. No other elements cause trouble.

It is necessary that the acetic acid be added to a solution not too alkaline, as the acetate formed on adding the acid to an alkaline solution decreases the ionization of the acetic acid (according to a well-known law) thus making the solution insufficiently acid for the reaction between the copper and the iodide to be complete, causing an indefinite end point.

If the end point is overrun, simply add 1 c.c. of a copper sulfate solution containing 0.01 gram of copper per cubic centimeter, then complete the titration and subtract 0.01 gram from the total amount of copper found.

When the ore contains arsenic or antimony, it is necessary to use bromine after the solution of the ore has been evaporated to sulfuric acid fumes, for even if the ore is dissolved in aqua regia, after evaporation to fumes of sulfuric acid the arsenic and antimony are present as the trivalent elements.

Short Iodide Method for Copper

The following process is a modification of the process of Mott.[1] The process is very rapid and according to the writer's experience the results obtained by its use are nearly as good as by the long iodide method.

The copper is not separated from the other metals. This makes it necessary to remove any ferric ions which, if present, would liberate iodine and cause results to be high. These ferric ions are removed by adding ammonium fluoride which forms with the iron undissociated ferric fluoride, which, since it is undissociated, has no oxidizing power and cannot liberate iodine under the conditions of the solution.

Process of Analysis.—Dissolve a sufficient sample of the ore in 5 c.c. of strong HCl and 7 c.c. of HNO_3, heating the solution to boiling. When action has ceased, add 10 c.c. of 1 : 1 H_2SO_4 and evaporate rapidly until the sulfuric acid fumes strongly. Cool and add 30 c.c. of water, heat until all soluble salts are in solution, then add 5 c.c. of bromine water and boil vigorously for 10 minutes or until all bromine has gone. Now add NH_4OH until ferric hydroxide persists on shaking, then add 2 or 3 c.c. of 80 per cent. acetic acid, cool to tap-water temperature, add 2 grams of HN_4F and stir until it is dissolved. The ferric hydroxide will immediately dissolve but the solution will be turbid. Add 2 grams of KI dissolved in water and titrate as usual.

[1] *The Chemist-Analyst*, July, 1912.

Notes on the Process.—The thiosulfate should be standardized by dissolving 0.20 gram of copper and about 0.10 gram of iron in nitric acid and treating the solution exactly like an ore solution.

After the titration is finished the solution should be emptied out of the beaker, as the beaker will be etched by the HF on long standing.

The writer has used this method on samples containing 10 per cent. of iron, 5 per cent. arsenic, and 7 per cent. antimony with perfect results when compared with the long iodide method.

The writer often combines the sulfocyanate precipitation with the thiosulfate titration.

References for the Iodide Method:

Peters, *J. Am. Chem. Soc.*, XXXIV, p. 422. Sources of error in standardization.

Videgren, *Z. anal. Chem.*, XLVIII, 539.

McClure, *Mining Sci. Press*, CIII, 48.

Lathe, *Eng. Mining J.*, XCIII, 1073. Methods used at Granby.

The Electrolytic Determination of Copper in Ores, Etc.

The electrolytic precipitation of copper is the most accurate method of determining of copper when the conditions are right. Ores containing arsenic, antimony, bismuth, or selenium or tellurium are perhaps not best analyzed by the electrolytic method. It is true that the electrolytic separation of copper from these elements can be made but the methods are not usable technically. So if these interfering elements are present they must be separated by purely chemical methods before the copper is electrolyzed. Methods involving delicate adjustment of potential for the separation of elements, while interesting from a scientific standpoint, are too troublesome to be used in technical analysis; the only electrolytic methods used are those in which separation depends upon choice of electrolyte; some elements will separate from acid solutions, some will not. Some will separate from sulfide solutions, some will not. Thus copper can be separated electrolytically from iron, aluminium, zinc, etc., from a dilute nitric or sulfuric acid solution.

The deposition of copper should take place from a solution free from hydrochloric acid (except under special conditions), free from interfering elements, and not too acid with either nitric or sulfuric acids. It is important that the current density at the cathode be not too great. The current density depends upon the size of the cathode, the distance between the electrodes, the conductivity of the solution and the drop of potential between the electrodes. If the current density be too great the copper will deposit in a non-adherent condition.

If the solution is kept vigorously stirred so that the copper ions are kept coming in contact with the cathode rapidly, the precipitation of the copper is more rapid and the current density employed may be much greater without getting a poor deposit. If a gauze cathode is used an enormously greater current density may be used than if a plain cathode be used. A plain flat cathode should be sand blasted or roughened in some way so that the copper deposit will be more adherent.

Method for Ores free from Arsenic, Antimony and Bismuth.— Use for a sample an amount of ore which will contain not more than 0.20 gram of copper. The sample must be finely ground. Put in a 150 c.c. beaker and add 15 c.c. of a mixture of equal parts of HNO_3 and HCl. Heat until decomposition of the ore is complete. Add 4 c.c. of H_2SO_4 and evaporate to copious fumes of SO_3. Cool, add 25 c.c. of water and 5 c.c. of HNO_3 and heat until all soluble salts are dissolved. Dilute to 125 c.c. and filter if the residue is such as not to settle clear. If it settles well it is not necessary to filter. The solution is now ready for electrolysis. If silver is present add just enough NaCl solution to precipitate it.

The details of the electrolysis will depend upon the nature of the cathode. If a plain electrode is to be used add 1 c.c. of the "nitro preparation,"[1] if a gauze electrode is used it is not needed. Connect to a suitable source of electric potential and adjust the rheostat until the proper current density on the cathode is attained. If a plain cathode is used the current density should be from 0.1 ampere to 0.5 ampere per 100 sq. cm. of surface, depending upon the roughness of the surface and amount of copper to be deposited. The rougher the surface and the less the copper present the greater the current density that may be employed. With a plain electrode the time required will be from four hours to over night unless the solution be continually stirred. If the solution be kept agitated the time required may be greatly reduced. If a gauze cathode be used the electrolysis may be completed in from 15 minutes to an hour with a current of 5 amperes without the trouble incident to a mechanical stirrer or solenoid and still beautiful and adherent deposits of copper are obtained.

[1] The "Nitro Preparation" is made by G. A. Guess as follows: Warm 10 grams of No. 4 hard oil or vaseline with 100 c.c. of strong HNO_3 until the action ceases, then dilute to 300 c.c. and filter.

The writer uses gauze cathodes and has abandoned mechanical stirring of the solution as being unnecessary and troublesome. If stirring of the solution be done, it is best to use a rotating magnetic field produced by a solenoid.

Continue the passage of the current until the copper seems all precipitated, then withdraw ½ c.c. with a pipette and add it to a similar amount of H_2S water on a paraffined white plate. (The liquid will not run on the paraffined plate.) If the slightest amount of copper remains the test will darken. If the test shows that the copper is all precipitated, lift the cathode quickly out of the solution and set in a beaker of distilled water. Then wash it with alcohol, dry on a steam plate or in an oven at about 100°, cool and weigh. The copper should be crystalline and beautifully bright and too firm to be scratched off with the finger-nail. If it is firm but dull in color it indicates the presence of one of the interfering elements. The precipitate should not be dried by moistening it with alcohol and setting fire to the alcohol as this causes some oxidation of the copper. The weight of the cathode and copper minus the weight of the cathode divided by the weight of the sample, then multiplied by 100 gives the percentage of copper in the sample.

References:

See Spillsbury, *Eng. Mining J.*, LXXXIV, 773. Short method using "nitro."

Guess, *Eng. Mining J.*, 1906, 328. Electrolytic assay for Pb and Cu.

Heath, *J. Ind. Eng. Chem.*, III, 73. Exact electrolytic assay of copper.

Traphagen, *Chem. News*, CIV, 69.

Caven and Chadwick, *Eng. Mining J.*, LXXXIX, 954. Electrolytic methods for slags, ores, mattes, and blister copper.

Benner, *J. Ind. Eng. Chem.*, II, 195, and *Met. Chem. Eng.*, IX, 141. Use of gauze cathode in technical analysis.

The source of the electric current may be a direct current power line or storage batteries or primary cells or an alternating current power line. If a direct current power line is used all that is necessary is a proper rheostat and ammeter in series with the electrolysis cell. If direct current line is not available but an alternating current is, it may be used in connection with a chemical rectifier or a motor generator set. Storage batteries are very convenient, especially when only alternating current

power is available and it is not desired to keep a rectifier running continuously. The writer uses a chemical rectifier in connection with alternating current to charge storage battery from which current for electrolysis is obtained. The rectifier cost about $10 to build and has been in service for several years with perfectly satisfactory results. It is shown in Fig. 13.

A–A–A–A are aluminium plates 10×4 in. in size. L–L–L–L are lead plates of the same size. These plates are attached to brass rods which pass through a hard rubber board, and are fastened by nuts to the bars B, C, D and E. To bar B are attached two aluminium plates, to bar C are attached a lead and an aluminium plate, to bar D are attached two lead plates, and to bar E are attached a lead and an aluminium plate. The alternating terminals are on the bars C and E. The direct current terminals are on the bars B and D. The plates hang in the jars J–J–J–J, which are filled with a saturated ammonium phosphate solution. The jars set in a tank of water to keep them cool. The alternating current impulses cannot pass through the solution from aluminium plates to lead plates, but can pass from lead plates to aluminium plates. Thus both of the alternating current impulses are sent in the same direction out from bar B, to do whatever work is desired, and returned through bar D. The alternating potential between C and E must not be greater than 25 volts.

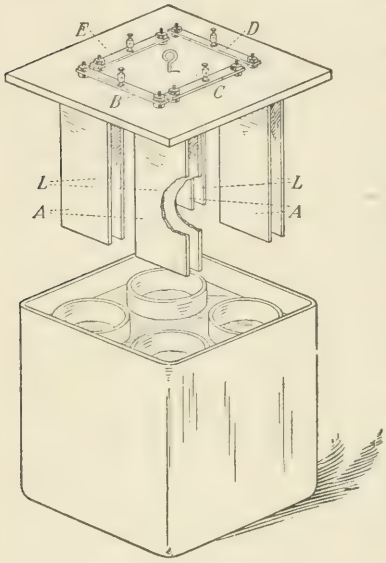

FIG. 13.

Method for Impure Ores.—Ores containing arsenic, antimony, or bismuth cannot be electrolyzed for copper without first separating the copper from these elements by purely chemical means. The following method makes the separation by one filtration and gives accurate results. It depends upon the fact that cuprous copper may be precipitated completely and free from the above elements by means of potassium thiocyanate (KCNS) from a solution slightly acid and containing tartaric acid. The CuCNS is dissolved and electrolyzed after the thiocyanic acid is destroyed.

Process of Analysis.—Dissolve a sufficient weight of the sample in 7 c.c. of HCl and 7 c.c. of HNO_3. When the ore is decomposed add 5 c.c. of H_2SO_4 and evaporate to fumes of H_2SO_4. Cool and add 25 c.c. of water in which is dissolved 3 grams of tartaric acid and heat until all soluble salts are in solution. Filter and wash the residue well with water. Add NH_4OH until the solution becomes alkaline, then add H_2SO_4 until the solution is acid, then 1 c.c. in excess. This makes the solution slightly acid with tartaric acid. Now add 2 grams of Na_2SO_3 to reduce the copper to the monovalent ion, heat nearly to boiling and add 1 gram of KCNS dissolved in water. The CuCNS precipitates immediately as a dense white precipitate but the solution will be colored red if there be trivalent iron present. This does no harm. Stir well and allow the CuCNS to settle for several minutes Then filter through a close filter and wash five times with a warm solution containing a little KCNS and tartaric acid.

Poke a hole through the paper and wash the precipitate through with a little water. Now pour through the filter 15 c.c. of a 1:2 HNO_3 solution. When the acid has run through, wash well with water but keep the volume of the filtrate down to at least 50 c.c. Now boil vigorously for 5 to 10 minutes to destroy the HCNS, cool, dilute to 125 c.c. and electrolyze, using a gauze cathode and a large current. The writer uses a gauze cathode of cylindrical form 1 in. in diameter and 2.5 in. high and a current of 2 amperes for 10 minutes, then a current of 4 amperes until the precipitation is complete as shown by a test on a white plate with H_2S. Precipitation is complete in one-half hour to an hour. Set the cathode quickly into a beaker of distilled water, then wash with alcohol, dry at 100° and weigh.

Notes on the Process.—The tartaric acid is added to keep antimony in solution and because the presence of tartaric acid is desired when the copper is precipitated. If the ore contains lead, the sulfate formed goes into solution when the tartaric acid is neutralized if it is not filtered off.

If the lead is in solution some of it precipitates when the sulfite is added and is left on the paper when the CuCNS is dissolved, but this does no harm as it precipitates on the anode during electrolysis, nor does the presence of large amounts of ferric iron. The writer has precipitated 0.2 gram of copper from 0.2 gram of iron, 0.1 gram of arsenic,

0.1 gram of antimony and 0.1 gram of bismuth and large amounts of lead and always obtained excellent results, correct almost to the limit of error of weighing on an ordinary analytical balance.

It is necessary to destroy the HCNS because the copper precipitates by electrolysis in a very spongy condition if there is HCNS in solution.

Instead of dissolving the CuCNS in acid and destroying the HCNS by boiling, the CuCNS on the paper may be ignited in a porcelain crucible until the paper is all burnt off and then the CuO formed dissolved in 5 c.c. of HNO_3, the solution diluted to 125 c.c. and electrolyzed.

Under the conditions given above one fully charged lead storage cell without a rheostat in series will give a drop of potential between the electrodes of 2 volts and a current of $\frac{2}{5}$ ampere. Two cells will give a drop between the electrodes of about 3 volts and a current of 3 amperes and three cells of 10 amperes capacity a drop of 3.5 volts and 5.5 amperes. So that when a gauze cathode is used a rheostat is not necessary to reduce the current.

Reference:

Demorest, *J. Ind. Eng. Chem.*, V, 216.

The Guess-Haultain electrolytic cabinets are made so that 200 or more determinations may be made in a day.

For the methods of electrolytic separation of copper from arsenic, antimony, bismuth, silver, mercury and other elements, see "Electroanalysis" by E. F. Smith and "Practical Methods of Electro-chemistry" by F. M. Perkin.

The Cyanide Method for Copper in Ores

When a nitric acid solution of copper is made alkaline with ammonia it becomes intensely blue owing to the formation of the compound $Cu(NH_3)_4(NO_3)_2$. When a solution of KCN is added to this blue solution it becomes less and less blue and finally colorless owing to the formation of colorless $K_3NH_4Cu_2(CN)_8$,[1] the copper thus changing from a part of a colored cation to a part of a colorless anion in which it is univalent.

The amount of KCN required to titrate a copper solution depends upon the temperature of the solution, the volume, the amount of ammonium salts and the amount of free ammonia present. Therefore to get good results these conditions must be the same when the copper from

[1] "Analytical Chemistry," Treadwell-Hall, Vol. I, p. 172.

the sample is titrated as when the KCN is standardized. This is absolutely necessary.

Any nickel, silver or zinc present will also be titrated with the KCN and so must be removed.

Process of Analysis.—Dissolve 1 gram of ore with 5 c.c. of HCl and 5 c.c. of HNO_3. Add 7 c.c. of H_2SO_4 and evaporate until the H_2SO_4 fumes copiously. Cool, add 30 c.c. of water and heat until all ferric salts are dissolved. Again cool and add 4 grams of pure granulated zinc and shake for five minutes. Heat until the zinc is all dissolved, then add 25 c.c. of H_2S water. Filter through a funnel, into the apex of which is stuffed a plug (made by shaking a mixture of equal amounts of glass wool and asbestos and then pouring in the funnel). Wash the precipitated copper until all zinc salts are removed, wash the copper back into the flask, place the flask under the funnel and pour through 10 c.c. of a hot 1:1 HNO_3 solution. Pour the same solution through several times, if necessary, to get all the copper dissolved. Finally wash well to remove all the copper nitrate. Do not use more than 10 c.c. of HNO_3, sp. gr. 1.10, in dissolving the copper.

Now boil to remove red fumes, dilute to 125 c.c. and if silver is present add a drop of HCl and filter off the AgCl. Add 10 c.c. of NH_4OH, sp. gr. 0.9, cool to room temperature and titrate.

Run in the standard cyanide solution *slowly* and with constant shaking until the blue color is almost gone.

The solution will now generally be turbid. Filter, wash once, dilute to 180 c.c., and carefully complete the titration by adding the cyanide drop by drop, shaking the solution after each drop until the blue tinge just disappears.

Standard Cyanide Solution.—Dissolve 21 grams of pure KCN and 2 grams of KOH in distilled water, dilute to 1 liter, and mix well. One cubic centimeter is equal to about 0.005 gram of copper. Now weigh accurately 0.2 gram of pure copper wire or foil and dissolve in a 250 c.c. Erlenmeyer flask with 10 c.c. of 1:1 HNO_3. Boil off the red fumes and dilute to 125 c.c. Add 10 c.c. of NH_4OH, cool to room temperature, and titrate with the KCN solution *slowly* until the blue is nearly gone. Now dilute to 180 c.c. and carefully finish the titration until the blue just disappears.

Notes on the Process.—The zinc used to precipitate the copper must be all dissolved. This can be told by the cessation of the effervescence. If the solution becomes too concentrated, $ZnSO_4$ separates out and stops the solution.

If the H_2S causes a precipitation of copper sulfide, the filter should be washed with 5 c.c. of bromine water after the copper has been dissolved with HNO_3. This dissolves the sulfide.

If the titration is made rapidly the blue color will persist even after enough HCN has been added to react with all the copper. This is because the reaction takes some time for completion. Hence the titration must be made slowly.

A concentrated solution requires more cyanide for decoloration than a dilute one. A hot solution requires less than a cold one. The amount of cyanide required is affected by the amount of ammonia or ammonium salts present. Hence the condition should be the same when the ore is titrated as when the cyanide is standardized.

The KCN solution keeps better when the KOH is added.

If only an approximate determination of the copper is desired, it can be made very rapidly by omitting the zinc precipitation. In this case treat 1 gram of the ore with 5 c.c. concentrated HNO_3, and boil till the copper is extracted and most of the acid driven off. Now add 5 c.c. more HNO_3, dilute to 125 c.c., add 10 c.c. of strong NH_4OH and run in the cyanide till the blue color is nearly discharged. Filter off and finish the titration as before. If there is a very large precipitate of $Fe(OH)_3$, repeat the process on a new sample of ore, adding nearly sufficient cyanide solutions as calculated from the first determination before filtering.

Sulfocyanate-Permanganate Method for Copper

As said on page 206, copper can be completely precipitated as CuCNS. When this precipitate is acted upon by a caustic alkali the following reaction takes place: $CuCNS+NaOH=CuOH+NaCNS$. The CuOH is left on the filter while the NaCNS goes into solution. The sulfocyanic acid is titrated by a standard solution of permanganate, the final results of the oxidation being expressed thus:

$$5HCNS+6KMnO_4+4H_2SO_4=3K_2SO_4+6MnSO_4+5HCN+4H_2O$$

That is, the sulfocyanic acid equivalent to 1 atom of copper requires 3 atoms of oxygen to oxidize it, which is the amount of oxygen required to oxidize 6 atoms of iron from divalent to trivalent condition. Then to get the copper value of the permanganate from the iron value we make

the following proportion, Cu : 6Fe : 63.57 : 335.04, or the iron value multiplied by 0.1897 gives the copper value of the permanganate.

When this titration is performed in acid solution the reaction is not strictly in accord with the above written one and an empirical factor must be used, raising the calculated value for the permanganate by about 5 per cent. When the titration is made in an alkaline solution, as described below, the titration takes place in accord with the above reaction and the iron value of the permanganate used multiplied by 0.1897 gives the amount of copper present. No elements interfere.

Process of Analysis.—Place 1 gram or a sufficient amount of the ore (or metal) in a 200 c.c. beaker, add 5 c.c. of HCl and heat a few minutes, then add 10 c.c. of HNO_3 and heat until the ore is decomposed. Then add 10 c.c. of 1:1 H_2SO_4 and evaporate to fumes of SO_3. Add 50 c.c. of water containing 3 grams of tartaric acid and heat until all soluble salts are dissolved. Filter and wash, cool and add NH_4OH until the solution becomes alkaline (or becomes deep blue). Then add H_2SO_4 until the liquid is acid, and then 1½ c.c. more of strong acid, sp. gr. 1.84. Heat nearly to boiling and add 1 gram of Na_2SO_3 dissolved in water and then pour in slowly and with vigorous stirring 1 gram of KCNS dissolved in 20 c.c. of water. Allow the beaker to remain on the hot plate at a nearly boiling temperature for some time to allow any tartaric acid carried down by the precipitate to dissolve. This is important.

Now allow the solution to cool somewhat and filter, preferably through asbestos, and wash a half dozen times with warm water. Set a clean flask under the funnel (or wash out the suction flask if one is used) and pour over the white precipitate 30 c.c. of a hot 10 per cent., solution of NaOH, and wash well with water.

Heat the filtrate to about 50° and run in, slowly at first and with constant stirring, standard permanganate solution. The liquid being titrated turns a green color. After an amount of permanganate has been added which judging from the amount of the CuCNS which was obtained is about half the amount necessary to finish the titration, test a drop for sulfocyanic acid by adding it on a white plate to a drop of ferric chloride strongly acid with HCl. If a deep red color remains after stirring the drops, continue adding the permanganate 5 c.c. at a time until a test gives a slight red color, then test after every 2 c.c. until a test shows almost no red indicating the absence of more than a trace of

sulfocyanic acid ion. Now add 30 c.c. of 1 : 1 H_2SO_4, stir the solution until all MnO_2 dissolves and then finish the titration to the usual permanganate end color.

Notes on Process.—If the ore does not contain lead it is not necessary to filter off the gangue. If it does, the lead sulfate must be filtered off, as it goes into solution in the ammonium tartarate and precipitates as lead sulfite with the CuCNS. Silver, if present in the ore, will precipitate as sulfocyanate but may be removed as AgCl with the lead.

The tartaric acid keeps antimony in solution. Not more than 3 grams should be used as a crystalline compound of tartaric acid tends to separate from the solution when it cools if too much is present. Hence not too much should be used and the solution should be kept hot.

It is essential that the precipitation of CuCNS be made just as directed as to acidity, stirring and digestion after precipitation.

After a little experience it is easy to tell how much permanganate it is safe to add before testing for sulfocyanic acid. But it does no harm to begin testing from the first after each, say, 5 c.c. of permanganate. One can tell from the depth of the red color obtained on testing with ferric chloride when one is nearing the end. When the test gives almost no red, it will still require several cubic centimeters of permanganate to finish the titration when the solution is made acid. The permanganate used is one of which 1 c.c. equals 0.01 gram of iron or 0.001897 gram of copper.

The writer prefers to filter the CuCNS on an asbestos mat either in a Gooch crucible or in a funnel containing a plug of glass wool, on which the asbestos fiber is sucked down tightly. If the filtering is done through paper the blank is increased. A blank should be made in any case to determine whether the NaOH contains oxidizable impurities. The blank should be almost nothing.

When the permanganate is added to the alkaline solution it turns green; on standing MnO_2 separates because the permanganate is reduced thus, $2\,KMnO_4 = K_2MnO_4 + 2O$. The oxygen oxidizes the sulfocyanate.

Reference:

Demorest, *J. Ind. Eng. Chem.*, V, p. 215.

Very excellent results can be obtained by dissolving the precipitate in 2 c.c. of strong nitric acid, boiling the solution for a few minutes to destroy all sulfocyanic acid, adding NH_4OH until the solution is alkaline, then making acid with acetic acid and determining the copper by the iodide titration. (See Tsukakoski, Eng. Mining J., XC, 969). This is the method the writer prefers on miscellaneous ore samples.

CHAPTER XXII

THE DETERMINATION OF LEAD IN ORES

Lead may be determined either gravimetrically or volumetrically. The electrolytic method is the most accurate one and is quite rapid. Lead ores are dissolved in about the same way as copper ores. The chief minerals are galena (PbS), cerrusite ($PbCO_3$), anglesite ($PbSO_4$).

The Electrolytic Determination of Lead

Lead is precipitated on the anode from a nitric acid solution as PbO_2. The precipitation is rapid owing to the high atomic weight of lead and the small solution tension of PbO_2 in nitric acid. The precipitated PbO_2 does not adhere well to a smooth flat electrode, but adheres well to a gauze electrode, so well in fact that it cannot be rubbed off with the finger.

If bismuth or antimony are present they will partially deposit with the lead, and manganese will also deposit as MnO_2 with the lead unless the solution is very acid. The presence of arsenic, selenium or tellurium will prevent the precipitation of the PbO_2 partially or wholly. If any of these are present they must be removed by chemical means, which is easily done. Phosphoric acid if present will prevent the precipitation of lead.

Process of Analysis for Ores Free from Arsenic, Antimony or Bismuth.—Weigh an amount of sample containing not more than 0.5 gram of lead. Put it in a 250 c.c. beaker, add 10 c.c. of strong HCl and heat to boiling for several minutes. Then when most of the sulphur is driven off as H_2S add 15 c.c of HNO_3 and continue the heating until the ore is all decomposed and finally boil vigorously to expel all chlorine. There must be no chlorine present during the electrolysis. Add 20 c.c. of water and then NH_4OH until there is considerable excess and heat until any lead sulfate is dissolved. Then add HNO_3 until there is 15 c.c. excess present, dilute to 100 c.c. and electrolyze, using a gauze anode. With a cylindrical gauze anode $\frac{3}{4}$ in. in diameter and

2½ in. high a current of 3 amperes and a potential of about 3 volts will cause complete deposition in 15 minutes to a half hour. It is best to electrolyze in a hot solution.

Break the current and set the anode in a beaker of pure water, then remove and dry at a temperature of 230° in an oven. Cool and weigh. Multiply the PbO_2 by 0.8640 to get the weight of the lead.

To remove the PbO_2 set the electrode in a beaker containing warm 1 : 3 HNO_3 and add a few cubic centimeters of alcohol or formic acid. The PbO_2 is reduced to PbO, which is soluble in nitric acid.

If the ore is soluble in nitric acid, the HCl may be dispensed with and the sample treated directly with the nitric acid. This will cause the formation of considerable lead sulfate which will dissolve when the solution is made alkaline and heated.

Method for Ores Containing Antimony or Bismuth.—Dissolve the ore as above directed and then add 5 c.c. of sulfuric acid and evaporate to very copious fumes of H_2SO_4. Cool and add 30 c.c. of water containing 3 grams of tartaric acid to keep the antimony in solution. Heat to boiling to dissolve all soluble salts, cool, filter and wash three times with cold water. Wash the lead sulfate back into the beaker with a small amount of water and pour through the filter into the beaker hot ammonium nitrate solution made by adding to 30 c.c. of 1 : 2 nitric acid 20 c.c. of NH_4OH. This will dissolve any lead sulfate left on the paper. Digest the solution in the beaker until the lead sulfate is all dissolved, then add nitric acid until there is 15 c.c. excess present, heat and electrolyze as above.

To test the purity of the deposit the following method is good: Place the anode in a beaker containing 40 c.c. of 1 : 3 nitric acid, add a few cubic centimeters of formic acid and heat until all PbO_2 is dissolved. Wash the anode, catching the washings in the beaker, add 5 c.c. of sulfuric acid and evaporate to copious fumes. Cool, add 30 c.c. of water and heat to boiling several minutes to change any lead bisulfate to sulfate. Cool, add 5 c.c. of alcohol, allow to settle and filter in a weighed Gooch crucible and wash several times with 10 per cent. alcohol. Ignite for five minutes at a barely visible red over a Bunsen burner. Weigh and multiply the weight of lead sulfate by 0.6830. Ores may also be analyzed

in this way if the analyst prefers to weigh lead sulfate instead of PbO_2. That is, the ore is dissolved as in the method for ores free from bismuth and electrolyzed. Then the PbO_2 (with oxides of bismuth and antimony and manganese possibly) is dissolved with nitric and formic acids and evaporated to copious fumes. Thirty cubic centimeters of water are then added and boiled, cooled, filtered and the lead sulfate washed with 10 per cent. alcohol. The Gooch crucible and the precipitate are heated for five minutes over a Bunsen burner, cooled and weighed. No elements interfere and very good results are obtained.

References:

Smith, "Electro Analysis."

Perkin, "Practical Methods of Electro-chemistry."

Benner and Ross, "Electrolytic Determination of Lead in Ores," *Mining Sci. Press*, CI, 642.

List, *Metal. Chem. Eng.*, X, 135.

Benner, *J. Ind. Eng. Chem.*, II, 348.

Woiciechowski, *Met. Chem. Eng.*, X, 108.

For the determination of lead by the molybdate method of Alexander see Low, "Technical Methods of Ore Analysis." This method is less reliable and no more rapid than the dichromate method and so is not given here.

For the permanganate method for lead, see Bollenbach, Chem. Ztg., XXXIII, 1142.

The Volumetric Chromate Method for Lead

The following method is the one devised by Guess and modified by Low and Waddell. Low says, "I find it more generally satisfactory than any other."

It depends upon the precipitation of lead chromate from an acetic acid solution, which is then dissolved in hydrochloric acid, potassium iodide added and the liberated iodine titrated with standard thiosulfate solution.

Solutions Required. Extraction Solution.—Make a cold saturated solution of sodium acetate and filter it. Dilute it with 2 volumes of water and add 30 c.c. of 80 per cent. acetic acid.

Hydrochloric Acid Mixture.—Make a cold saturated solution of NaCl and filter it. To 1 liter of the salt solution add 250 c.c. of water and 100 c.c. of hydrochloric acid, sp. gr. 1.2.

Potassium Dichromate.—Make a cold saturated solution of the commercial salt and filter it.

Starch Solution.—Make as directed on page 100.

Process of Analysis.—Weigh 0.5 gram of the ore and put it into a 150 c.c. flask. Add 10 c.c. of strong HCl and heat until no more H_2S comes off. Add 5 c.c. nitric acid and boil until the ore is completely decomposed. Now add 10 c.c. of 1:1 sulfuric acid and boil until copious white fumes come off. Cool, add 50 c.c. of water and heat to boiling until all the soluble salts are dissolved, cool and add 5 c.c. of ethyl alcohol, allow to settle, then filter through a 9 cm. filter and wash with cold 10 per cent. sulfuric acid solution five times and then twice with water.

Have the extraction solution nearly boiling, and with a fine jet wash the lead sulfate back into the flask, then wash the filter thoroughly with the hot solution until all lead sulfate remaining on it is dissolved, catching the washings in the flask containing the rest of the lead sulfate, and taking care to wash under the folds of the filter paper. Heat the filtrate to boiling and add more of the acetate solution if necessary to dissolve all of the lead sulfate. Finally dilute to 150 c.c., heat to boiling, add 10 c.c. of the dichromate solution and boil for seven minutes. It is necessary to boil about this length of time to insure always the same constitution of the lead chromate. Now filter through a large filter paper and wash the flask and precipitate ten times, with a hot solution of sodium acetate made by diluting 50 c.c. of a cold saturated solution to 1 liter. Place the clean flask under the funnel, and with a jet of the cold HCl mixture dissolve the precipitate on the filter. Continue the washing and stirring up the precipitate with the HCl mixture until all the residue and all color are removed from the filter. Use at least 50 c.c. of the mixture.

Now add 4 c.c. of a 25 per cent. solution of KI and titrate at once with standard sodium thiosulfate solution. Continue adding the thiosulfate until the brown color of the liberated iodine becomes faint; then add enough starch solution to produce a strong blue color and continue the titration until the solution becomes a pale green with no tinge of blue. The end point is very sharp.

Standardize the thiosulfate solution on pure lead. The reactions in the determination are:

$$2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2.$$

$$2H_2CrO_4 + 6KI + 12HCl = 6KCl + 2CrCl_3 + 8H_2O + 6I.$$

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_4.$$

Therefore one Pb equals one H_2CrO_4 which liberates 3I, which equals $3Na_2S_2O_3$. That is, to titrate the iodine liberated by the H_2CrO_4 from one Pb requires $3Na_2S_2O_3 \cdot 5H_2O$. Then to make a solution of thiosulfate, 1 c.c. of which will equal 0.005 gram of lead, will require for 1 liter the amount of thiosulfate indicated by the following proportion: $Pb : 3Na_2S_2O_3 \cdot 5H_2O :: X : 5$, or 17.985 grams per liter. The thiosulfate solution used for the copper determination will do. To standardize, dissolve about 0.2 gram of pure lead in 15 c.c. of 1:2 nitric acid, add 5 c.c. of sulfuric acid and evaporate to strong H_2SO_4 fumes and treat as above directed for an ore.

Notes on the Process.—As a fungus growth forms in the acetate wash, only enough to last a day should be made unless it is heated frequently.

If the end point be passed in titrating, a few drops of a standard dichromate solution may be added and the titration finished. The iron value of the dichromate multiplied by 1.2363 gives the lead value.

The constitution of the lead chromate depends upon the temperature, acidity and concentration of the solution and the precipitation of the lead from the ore must be made exactly as it is made in the standardization of the thiosulfate.

Bismuth in small amount does not interfere but if there is much in the sample some may remain as sulfate with the lead. In such a case just before filtering off the lead chromate add 2 grams of citric acid dissolved in a little hot water. This will dissolve any bismuth chromate present.

If the ore contains barium it is difficult to extract all the lead sulfate with the acetate mixture. In such a case after the acetate has been used, drop the filter in a flask, add 10 c.c. of strong HCl and boil almost to dryness, add 25 c.c. of the acetate solution, boil vigorously and filter and wash; the combined filtrates are then treated as usual.

Wilder's Modification.—Treat 0.50 gram of ore as is usual for lead ores up to the point where the washed sulfate is obtained on the filter paper. Remove the paper from the funnel and fold lengthwise in such a manner that it can be introduced into a 200 c.c. graduated flask. Place a few grams of sodium acetate and 1 c.c. of acetic acid in the flask and add about 50 c.c. of water. Then place the flask on the hot plate until the lead sulfate is all in

solution. This may be hastened by shaking to break up the filter paper.

Now run in an excess of standard dichromate solution from a burette, and after mixing by shaking, make the contents up to the mark by adding water. Invert the flask ten times with the hand over its mouth to mix thoroughly. Take three No. 589 S. & S. filters, fold as one and place in a dry funnel with a dry 100 c.c. flask beneath. Filter 100 c.c. and transfer to an Erlenmeyer flask.

Add a few cubic centimeters of sulfuric acid, enough potassium iodide to react with the excess of chromic acid and titrate with sodium thiosulfate in the usual manner, using starch indicator. The standard dichromate contains 3.558 grams of dichromate per liter. The thiosulfate theoretically contains 8.8177 grams per liter, but 9.150 will be more apt to give the desired strength.

Making the solutions this way, 1 c.c. of dichromate should equal 1 per cent. of lead and 2 c.c. of thiosulfate. Therefore subtracting the cubic centimeters of thiosulfate used from the cubic centimeters of dichromate used will give the per cent. of lead direct, without any further calculation.

Notes on the Method.—The chromate solution and the thiosulfate solution are both stable, and once standardized will not require further attention for a month or more. They may be titrated against each other occasionally and restandardized if any variation is found.

The lead chromate precipitate is fine unless boiled, and therefore three filter papers are used. The solution filters quickly, however. In methods where the solution is boiled the lead chromate is of variable composition, depending upon the conditions of precipitation, basic chromates being formed. This method avoids any washing of the chromate and thus saves time and avoids errors due to washing.

References:

Low, "Technical Methods of Ore Analysis."
Guess, *Trans.* Am. Inst. Mining Engrs., XXXV, 359.
Waddell, *J. Ind. Eng. Chem.*, III, 638.
Wilder, *Eng. Mining J.*, XCII, 390.

CHAPTER XXIV

THE DETERMINATION OF TIN IN ORES

Tin occurs in ores generally as SnO_2 (Cassiterite), sometimes as SnS_2 (Stannite). Cassiterite is insoluble in all acids, and to get the tin in solution it is necessary either to fuse the ore with an alkali, forming a stannate which is soluble in acids or to reduce the SnO_2 at an elevated temperature with either a reducing gas as illuminating gas or with finely divided metal as powdered zinc or aluminium. When the amount of tin is very low and a large sample is used, the reduction of the SnO_2 with a powdered metal to metallic tin followed by solution of the tin in hydrochloric acid is best, because if a large sample is fused with an alkali and the fusion dissolved in acid, the liberated silicic acid causes trouble in filtration. A solution of stannic chloride in hydrochloric acid should not be evaporated as stannic chloride boils at 114°C.

Tin may be determined gravimetrically by weighing as SnO_2 after precipitation as metastannic acid, or by weighing as the metal after electrolytic precipitation, or volumetrically by titrating the tin in stannous state by a standard oxidizing solution, preferably iodine.

Stannous salts take up oxygen really from the air, consequently the solution, which is to be titrated, must be protected from the air by a neutral gas as carbon dioxide.

The following process is the well-known one of Pierce and Low with the reduction and titration carried out as directed by Patrick and Wilsnack. It depends upon reducing the tin in a strong hydrochloric acid solution in absence of air by means of the combined action of metallic iron and antimony. The tin is reduced to $SnCl_2$, which is then titrated with iodine solution, thus, $SnCl_2+2I+2HCl=SnCl_4+2HI$.

Process of Analysis.—Place in an iron crucible about 8 grams of sodium hydroxide or 5 grams of sodium peroxide and heat over a Bunsen burner until the charge is melted. Cool and add a gram of the finely ground ore. Cover the crucible and heat cautiously to prevent spattering and finally heat with the full flame of the Bunsen until the fusion is quiescent and keep the mass thus fused for about a half hour to insure complete solution of the cassiterite. Cool and dissolve the cake in about 50 c.c. of

water and enough HCl to neutralize all the NaOH and add 50 c.c. additional. When all is in solution, transfer the solution to a 500 c.c. Erlenmeyer flask and add 5 c.c. of sulfuric acid in which is dissolved 0.1 gram of antimony.

Close the flask with a three-hole rubber stopper. Through one hole put a piece of glass tubing reaching to the bottom of the flask, through another place an iron rod the end of which is coiled into a spiral. The rod should fit loosely enough to slip up and down in the hole in the stopper, and be long enough to have the spiral reach to the bottom of the flask while the other end sticks out of the stopper several inches.

Push the iron spiral down in the solution and pass CO_2 or natural gas (freed from H_2S by passing through NaOH) through the glass tube until the air is driven out of the flask and then boil the solution for 25 minutes while continuing the current of gas. Cool the flask while a rapid current of gas passes through to prevent air entering. When the solution is cold raise the iron coil out of the liquid, wash it by squirting a jet of recently boiled cold water through the third hole in the stopper, put in 4 c.c. of starch solution and then titrate the tin with standard iodine solution by introducing the tip of the burette through the hole in the rubber stopper and running in the iodine solution until a drop turns the starch blue. The iron coil must be so placed that the iodine solution does not drop on it.

Notes on the Process.—When near the end point, which is told by the slow disappearance of the blue color of starch iodide, the titration should proceed slowly to prevent overrunning the end point.

Large amounts of copper, lead, nickel, and perhaps other metals interfere with the accuracy of the titration if they are present and ores containing them should be first treated with aqua regia, evaporated to dryness, digested with hydrochloric acid and filtered. The residue on the paper is then treated for tin as above directed.

Arsenic and antimony when in trivalent condition consume iodine if the solution is weakly acid but in the strong acid solution as used in this process they are without effect.

The reduction of the tin is not complete if only iron is used or if only antimony is used but is perfect if both are used.

Iodine Solution.—To make the iodine solution, put 20 grams of KI and 50 c.c. of water in a liter flask and then add 12.7 grams

of pure iodine, stopper the flask and shake the solution until the iodine is all dissolved. Then dilute to a liter and mix well. Standardize against c.p. tin, by dissolving 0.2 gram in a flask in 50 c.c. water and 50 c.c. strong HCl. When dissolved add 5 c.c. of sulfuric acid containing 0.15 gram of antimony and reduce and titrate as directed for the ore. Iodine solution of the above strength is tenth-normal and should equal 0.00595 gram of tin per cubic centimeter.

The results obtained are accurate to 0.2 per cent. when as much as 0.5 gram of tin is present and much more accurate with the small amounts of tin found in ores.

References:

Low, "Technical Methods of Ore Analysis," p. 247.

Patrick and Wilsnack, *J. Am. Chem. Soc.*, IV, 597.

Gray, *J. Chem. Met. S. Africa*, X, 312.

Morgan, *Chem. Eng.*, XIV, 289.

Lewis, *London Mining J.*, 1911, 606, *J. Chem. Met. S. Africa*, XII, 32. The electrolytic determination of tin.

CHAPTER XXV

THE ANALYSIS OF REFINED COPPER

The properties of copper are greatly affected by the presence of small amounts of impurities. The most common impurities are arsenic, antimony, oxygen, bismuth, lead, iron, sulfur. Also silver and gold are often present in considerable amounts, while silicon, aluminium, nickel, cobalt, selenium, phosphorus and tellurium may be present.

The following method for arsenic and antimony is as described by Heath.[1] It depends upon the precipitation of the antimony and arsenic from the solution of the copper by adding a sufficient amount of ferric salt and then NH_4OH. The ferric hydroxide carries down with it the arsenic and antimony in combination with the iron. The arsenic and antimony are separated from the iron by hydrogen sulfide, the sulfides are dissolved in sodium sulfide, the arsenic and antimony oxidized to pentavalent form by fuming nitric acid. Arsenic is separated from antimony by precipitating it out as sulfide from 2 : 1 hydrochloric acid solution in which antimony sulfide is soluble.

Process of Analysis.—Dissolve 25 grams of the drillings in a 600 c.c. beaker with 110 c.c. of nitric acid, sp. gr. 1.42. Dilute to 300 c.c. and add a solution of 2 grams of c.p. ferric sulfate made from c.p. crystallized ferrous sulfate. Heat nearly to boiling and add NH_4OH until the iron is precipitated and the copper salts redissolved. This will take about 175 c.c. Heat to boiling, let settle a half hour on a hot plate and filter on a 15 cm. ashless paper. If bismuth is to be determined add 2 grams of ammonium carbonate and 5 c.c. of saturated sodium phosphate solution after the iron is precipitated. If the copper contains more than 0.1 per cent. of arsenic and antimony add more of the ferric sulfate to the acidified filtrate and again precipitate with NH_4OH, filter and wash both precipitates well with hot 1 : 10 NH_4OH. Redissolve the precipitate or precipitates with dilute sulfuric acid, precipitate again with NH_4OH, filter and wash well.

[1] Heath, *J. Am. Chem. Soc.*, III, 74.

Dissolve the ferric hydroxide with hot dilute sulfuric acid containing 5 per cent. of hydrochloric acid and precipitate in the cold the arsenic, antimony and bismuth with hydrogen sulfide, passing the gas through for 15 minutes. Stopper the flask and let settle over night. In the morning pass hydrogen sulfide through again, filter on a small filter paper and wash with slightly acid hydrogen sulfide water.

Transfer the paper and contents to a small beaker and dissolve the sulfides of antimony, arsenic and tin with hot sodium sulfide, digesting until they are all dissolved. Use as little sodium sulfide as possible. Filter and wash with slightly alkaline hydrogen sulfide water. Bismuth sulfide remains on the filter.

To the filtrate add 0.2 gram of sodium hydroxide, evaporate to dryness on a steam plate, treat the residue with 20 c.c. of strongest fuming nitric acid and digest until the sulfur is all dissolved. Evaporate to dryness again.

Dissolve the residue in 35 c.c. of hydrochloric acid containing two parts of hydrochloric acid, sp. gr. 1.2, to one of water, adding a crystal of tartaric acid. Pass hydrogen sulfide through the cold solution until the solution is saturated, whereupon the arsenic precipitates. Allow to settle a short time, filter on an asbestos mat, and wash with acid of the same strength as the solution. Wipe out any sulfide adhering to the side of the beaker with asbestos. As soon as the mat is washed well the beaker is removed and the acid removed from the mat with H_2S water. Test the filtrate with more hydrogen sulfide gas. Keep the filtrate for the antimony.

Digest the mat with the sulfides in a small beaker with fuming nitric acid, dilute with one and one-half times its volume of water and filter, wash, and evaporate to dryness with 0.1 to 0.5 gram of sodium nitrate according to the amount of arsenic present.

Dissolve the residue in 5 c.c. of cold water, 10 drops of hydrochloric acid and 0.1 gram of tartaric acid. Filter through a small paper and wash with the smallest amount of water possible. Make slightly alkaline with NH_4OH, when the volume should not be more than 12 c.c. Add 3 c.c. of magnesia mixture, make up to 20 c.c. with strong NH_4OH and stir five minutes. If the amount

of arsenic is excessive add more precipitant and increase the volume to 30 c.c., one-third of which is NH_4OH.

Allow to stand over night in a cool place, filter on a 3 cm. filter paper and wash with a fine jet of 1 : 3 NH_4OH until free from chlorine. Dry the paper in an oven, crumble out the arsenate on a glazed paper and put the paper in a porcelain crucible. Add a few drops of saturated ammonium nitrate and char the paper very carefully, add more nitrate and again heat carefully until the paper is consumed without giving an odor of arsenic. Add the rest of the arsenate, ignite at a full red heat and weigh. Or filter the arsenate on a small weighed Gooch filter, wash well, ignite and weigh as $Mg_2As_2O_7$, which contains 48.27 per cent. As.

The magnesia mixture should be free from lime and should not be used after it has attacked the glass of the bottle. It is made of one part of magnesium sulfate, four of ammonium chloride, eight of water and four of ammonia, sp. gr. 0.90.

Instead of determining the arsenic gravimetrically it may be titrated. Transfer the solution of arsenic sulfide in fuming nitric acid to a Kjeldahl flask, add 15 c.c. sulfuric acid and 3 grams $KHSO_4$ and evaporate to fumes for 15 minutes. Cool, add 0.5 tartaric acid and fume until colorless. Cool, dilute to 200 c.c. and add NH_4OH until just alkaline, then make just acid, add 3 drops of 10 per cent. KI and 10 grams $NaHCO_3$, cool and titrate with iodine. The solution is made as directed on page 225.

Antimony.—The filtrate from the arsenic sulfide contains the antimony (and traces of tin). Evaporate nearly to dryness to remove the excess of acid, dilute to 25 c.c. and precipitate the antimony (and tin) with H_2S. Filter, dissolve with a little sodium sulfide (to remove traces of copper), filter again, make the filtrate acid and pass in H_2S. Filter on a weighed Gooch filter, wash with H_2S water, ignite and weigh as Sb_2O_4.

If the determination of tin is desired it is separated from the antimony in the filtrate from the arsenic sulfide by Clark's oxalic acid method.

Bismuth.—The sulfide of bismuth left after the treatment of sulfides of arsenic and antimony with Na_2S is digested with 10 c.c. of nitric acid until dissolved, filtered, 1 c.c. of sulfuric acid added and evaporated to strong fumes to expel all nitric acid.

Dilute to 50 c.c., add sulfurous acid and 10 c.c. of dilute KI solution, boil off any free iodine, filter if necessary and dilute to 100 c.c. in a graduated flask. According to the depth of color take 10 c.c., 20 c.c. or 50 c.c. and transfer to a Nessler tube. Add a few cubic centimeters of dilute sulfurous acid. Into another tube put as much KI solution as in the assay tube, add sulfurous acid and then dilute to within a few cubic centimeters of the same bulk. Then add standard bismuth solution until the tints are the same. The color is due to the formation of bismuth iodide.

The standard bismuth solution is made as follows: Dissolve 0.1 gram of bismuth in a few drops of nitric acid, evaporate to fumes with 2 c.c. of sulfuric acid and dilute to 1 liter. The sulfurous acid used is made by diluting 10 c.c. of commercial acid to 1 liter.

One must be careful not to confuse the yellow color of free iodine with that of bismuth iodide. If the yellow color is removed by boiling and returns on standing it is due to free iodine. Hence the necessity of having a little sulfurous acid present to remove the iodine. But a strong solution of sulfurous acid will liberate iodine in the presence of H_2SO_4.

There should not be more than 1 mg. of bismuth in the tube or less than 0.1 mg. No elements interfere.

Selenium and Tellurium.—If these are wanted they are precipitated before the arsenic, antimony, and bismuth by passing SO_2 through the acid solution. This precipitates out the elementary selenium and tellurium. Filter them on a small Gooch mat, wash with water containing a little HCl and SO_2, dry at 104°C., weigh, ignite and weigh again.

Starch Indicator.—Starch prepared as follows is much more sensitive to iodine than when prepared in the ordinary way. When this indicator is used it is more accurate to titrate arsenic than to weigh it.

Allow the raw starch to stand for 24 hours in very dilute HCl, filter, wash, dry for three hours in an oven at 100°C. Boil 1 gram with 100 c.c. of water and filter.

Iodine Solution.—Dissolve 3.386 grams of pure iodine in 7 grams of KI and a little water and dilute to 1 liter. The end point in the titration is clearer if three drops of a 10 per cent. solution of KI are added after the $NaHCO_3$.

Lead, Iron, Nickel, Cobalt and Zinc.—Dissolve 50 grams of the copper in a mixture of 80 c.c. sulfuric acid, 50 c.c. nitric acid and 400 c.c. of water. Dilute to 600 c.c. and precipitate the copper on a large perforated platinum cylinder, using an 11×11 cm. cathode and a current of 3 amperes and preferably a rotating anode or a solenoid to rotate the solution. When the copper is all deposited, as shown by a test of a few cubic centimeters on a white plate with H_2S, evaporate the solution to a small volume, then transfer to a casserole and heat to fumes to remove the free sulfuric acid and most of the ammonium salts. The residue is dissolved in water and any lead sulfate and silica are filtered off. Hydrogen sulfide is then passed through the acidified filtrate and the precipitate filtered off and washed with hydrogen sulfide water. The precipitate is extracted with a little hot dilute sodium sulfide and the residue combined with the other precipitates containing lead, and the lead determined in them by electrolysis including the lead originally deposited on the anode as peroxide.

The main solution (volume about 50 c.c.) is oxidized and the iron precipitated with NH_4OH. Aluminium of course also precipitates.

The filtrate is acidified with acetic acid and 1 c.c. of strong acetic acid is added in excess. Heat to boiling and pass hydrogen sulfide through. Filter off the ZnS, ignite and weigh as oxide. Make the filtrate alkaline with NH_4OH and precipitate the nickel and cobalt with H_2S, filter and ignite and weigh as oxides. Nickel and cobalt may be separated with dimethylglyoxime. (See page 138 et seq.)

Determination of Gases in Copper

Pure CO_2 has no chemical action on red hot copper. If copper drillings are heated red hot in a current of pure CO_2, the occluded gases are driven out and the loss in weight is the weight of these gases which were in the sample. If the sample is then heated in a stream of hydrogen, the combined oxygen in the copper is driven out in the form of water, but some hydrogen remains in the copper. This may then be driven out by igniting again in a stream of CO_2 and the loss in weight is oxygen and sulfur. The sulfur driven off is determined by passing the hydrogen, after it leaves the tube, into cadmium chloride solution and then titrating with iodine solution.

Process.—Produce CO_2 in a generator from pure sodium bicarbonate, or marble, and HCl. Purify the CO_2 by passing it through a train of the following reagents: (A) Saturated $KMnO_4$ solution. (B) Solution of silver sulfate. (C) Concentrated sulfuric acid. (D) A tube of dry chromous chloride. (E) Stick phosphorus. (F) Calcium chloride. (G) Phosphorus pentoxide. Also make pure hydrogen in a Kipp generator and purify the hydrogen by the following train: (A) KOH solution. (B) Strong sulfuric acid. (C) Palladiumized asbestos tube heated red hot. (D) Soda-lime. (E) Calcium chloride. (F) Phosphorus pentoxide. The exit ends of the CO_2 train and the hydrogen train should be connected to a "T" tube, to the other end of which is attached the ignition tube.

Put 50 grams of fine drillings in the ignition tube and weigh the tube and drillings. Attach the tube to the "T" and pass CO_2 through until all the air is driven out (about 30 minutes). Then heat the tube red hot for 30 minutes while a rapid stream of CO_2 is passing. Cool the tube, without stopping the CO_2, and when cool displace the CO_2 with air by aspirating air through. Weigh. The loss in weight is occluded gases.

Again connect the ignition tube to the "T" and pass in hydrogen for 15 or more minutes, then keep at a red heat for an hour or more, depending on the fineness of the drillings. The exit hydrogen must be passed through an ammoniacal $CdCl_2$ solution. After the hydrogen has been passed through long enough, shut it off and pass the CO_2 through the tube until the hydrogen is all displaced (at least 20 minutes). Cool the tube and, when cool, displace the CO_2 with air and weigh. The loss in weight is oxygen plus sulfur. Titrate the sulfur with iodine as directed on page 105. Subtract the weight of sulfur from the loss in weight to get the weight of oxygen in the sample.

Great care must be used to have the surface of the copper from which the drillings are taken perfectly clean and free from grease, etc.

The H_2O found may be caught in P_2O_5 and weighed. See determination of oxygen in steel, page 181.

References:

Heath, *J. Ind. Eng. Chem.*, IV, 402.
Keller, *Trans.* Am. Inst. Mining Eng., XLVI, 764 (1914).
Brownson, *Trans.* Am. Inst. Mining Eng., XLVI, 757 (1914).

Sulfur.—The only rapid and exact method which has appeared in print for the estimation of traces of sulfur in the refined product is the following, which depends upon the removal of the copper from its solution in pure nitric acid by electrolysis. The solution, freed from copper, is gradually transferred to a No. 3 A casserole and evaporated to dryness over an alcohol flame with the addition of a little sodium carbonate to retain the sulfuric acid. The remaining nitric acid is removed by two evaporations with hydrochloric acid. A little HCl and 25 c.c. of water are added and the solution filtered. If any lead sulfate is found on the filters, they are boiled with a little sodium carbonate to render the sulfuric acid soluble, and filtered. The filtrates are combined and are then ready for precipitation by barium chloride. A blank analysis must be run with the acids and distilled water, which will usually show about 1 mg. of barium sulfate. When the copper contains much sulfur, it is necessary to use aqua regia for its solution, and to remove the hydrochloric acid by subsequent evaporations with nitric acid.

Reference:
Price and Mead, "Brass Analysis."

CHAPTER XXVI

ANALYSIS OF REFINED LEAD

Process of Analysis.—Clean 100 grams of lead, and hammer or roll into thin plates, being very careful to use a perfectly clean and bright hammer and anvil to avoid introducing iron into the sample. Dissolve the lead in a large beaker on the hot plate in 100 c.c. nitric acid, sp. gr. 1.42, and 250 c.c. water. If the solution gets too hot, it will foam very much and run over, consequently it is necessary to watch it until most of the lead is dissolved. For the same reason, hammering or rolling the lead into very thin strips is not desirable.

After all the lead is dissolved the solution is generally perfectly clear, although if more than 0.02 to 0.03 per cent. of antimony or tin is present it will show some turbidity. Dilute the solution to nearly 500 c.c. to prevent lead nitrate from crystallizing out on cooling. If not perfectly clear, filter. Add 30 c.c. concentrated sulfuric acid previously diluted with water, and shake the flask. After settling, pour off the clear solution and wash the precipitate several times by decantation.

Evaporate the solution to fumes of H_2SO_4, take up with 50 c.c. of water and filter off the lead sulfate through the paper containing antimony and tin. Digest the lead sulfate with pure sodium sulfide solution, filter and add the other sodium sulfide solution obtained further on. Treat the filtrate from the lead sulfate, while hot, with H_2S for some time and pass the gas through until cold. After settling completely, filter, determine the iron and zinc in the filtrate, and treat the sulfides with Na_2S. Determine antimony and arsenic as described under copper analysis.

The insoluble sulfides of lead, bismuth, copper, and silver may be dissolved in nitric acid, neutralized with sodium carbonate, and KCN added. Filter off lead and bismuth carbonates, acidify the filtrate with H_2SO_4 under the hood, filter off the AgCN and boil the solution to expel all HCN, after which determine the copper in the solution as follows:

Nearly neutralize the solution with NH_4OH, keeping the bulk small, say 50 c.c., add ammonium acetate, and divide into two equal parts. Add to one-half a fair excess of potassium ferrocyanide solution, and filter off the red precipitate immediately, passing through the paper twice if necessary. Add 1 c.c. acetic acid to each and the same amount of potassium ferrocyanide to the unfiltered half, and match the color in the filtered half by adding a weak copper sulfate solution of known strength from a burette, allowing one minute between each addition of copper sulfate for the color to develop.

Reference:
Crook's "Select Methods of Chemical Analysis," p. 338.

The silver cyanide precipitate is not desired, for silver is determined by cupelling a separate sample of the lead.

To determine bismuth, dissolve the carbonates of lead and bismuth in dilute nitric acid and precipitate as BiOCl, by Ledoux's method, thus. Nearly neutralize the nitric acid with NH_4OH, dilute to 300 c.c., complete the neutralization, add $\frac{1}{3}$ c.c. HCl, and heat nearly to boiling for an hour. Filter on a weighed Gooch crucible, wash with hot water, dry at 100°C., and weigh as BiOCl containing 0.8018 bismuth.

Notes on the Process.—To be sure of the results it is necessary to run a check analysis on the nitric and sulfuric acids, evaporating the same amount of them nearly down to dryness, and treating the last of the sulfuric acid in the same way as the lead sample.

The results of refined lead analysis are apt to depend more upon the chemist than on the lead, and it is desirable that as many errors as possible be eliminated in order to get accurate results. One of the sources of error is in the chemicals used, which are not absolutely pure and import certain quantities of iron, copper, arsenic and antimony. The amount of nitric and sulfuric acids used is as great as the lead sample, so that a check should be run on the acids.

Reference:
Betts, "Lead Refining by Electrolysis."

If bismuth alone is wanted, use the following method of Ledoux as given in Low's "Technical Methods of Ore Analysis," page 56.

Dissolve 25 grams of the lead in 200 c.c. of water and 40 c.c. of nitric of 1.42 sp. gr. Warm gently until all lead is dissolved,

then add 1:2 NH_4OH, very cautiously, finally drop by drop, until the free acid is gone and the liquid remains slightly opalescent. Now add 1 c.c. of 1:3 HCl. The solution will clear for a moment, then if there is an appreciable amount of bismuth present a crystalline precipitate of BiOCl will form. Heat nearly to boiling for an hour. Filter and wash the precipitate twice with boiling water. The precipitate will be contaminated with some lead and antimony. Dissolve it in a small amount of hot 1:3 HCl, wash the filter with hot water and dilute the filtrate with water, taking care that the dilution is not so great as to cause the precipitation of BiOCl. Pass H_2S through to precipitate the lead, bismuth and antimony as sulfides, filter, wash once with water, then with warm $(NH_4)_2S$ to dissolve the antimony sulfide, wash again with water and dissolve the bismuth and lead sulfides by placing filter and contents in a small beaker and heating with 1:4 nitric acid. Boil to disintegrate the paper and then filter and wash well with warm dilute nitric acid. Nearly neutralize the filtrate with NH_4OH, dilute to 300 c.c., complete the neutralization, and add 1 c.c. of 1:3 hydrochloric acid. Keep hot for an hour, filter on a weighed Gooch crucible and wash with water, dry at 100°C., and weigh as BiOCl containing 80.18 per cent. bismuth.

Bismuth may be determined in copper in the same way. The following is an analysis of refined lead in percentages:

Cu	Sb	Bi	Ag	Fe	Zn	Ni
0.0004	0.0008	0.002	0.0005	0.0006	0.0008	0.0007

CHAPTER XXVII

THE ANALYSIS OF BEARING METALS

Bearing metals are alloys selected for bearing linings on account of their combination of antifrictional properties with sufficient compressive strength to prevent them from being squeezed out of place under high compression, and strength to avoid breaking under heavy shock.

They are usually composed of lead, tin, antimony and copper in about the following proportions: lead 70 per cent., tin 15 per cent., antimony 15 per cent., copper 0 to 6 per cent. Journal brasses are composed of lead about 15 per cent., tin about 10 per cent. and copper about 75 per cent.

There are innumerable methods of analyzing alloys of lead, tin, antimony and copper, but the following method has given the writer the best results with a moderate expenditure of time.

When the alloy is digested with sulfuric acid under proper condition, the tin, antimony and copper all go in solution and the lead remains as insoluble lead sulfate. In the filtrate the antimony is found as $Sb_2(SO_4)_3$, the arsenic as $As_2(SO_4)_3$, and the tin and copper in their "ic" states. The arsenic is distilled off and titrated with iodine, antimony is titrated to the pentavalent state by standard permanganate and the copper precipitated as sulfocyanate after the antimony is titrated. Tin is determined in another sample in the filtrate from the lead sulfate either with or without a previous titration of the antimony. The results obtained are excellent and the time and attention required slight. If copper is not wanted, lead, antimony and tin can be determined on the same sample.

Process of Analysis.—Place 1 gram of the fine drillings or shavings in a Kjeldahl flask, add 10 c.c. of sulfuric acid, sp. gr. 1.84, heat the flask over a bare flame and keep the sulfuric acid at or near boiling until the residue in the flask is pure white. Cool, add 20 c.c. of water all at once to the sulfuric acid, boil for several minutes, allow the lead sulfate to settle a few minutes, cool to about 50°C., and pour the clear liquid through a weighed Gooch crucible with an asbestos mat, without allowing the lead sulfate to pass out of the flask. Put 10 c.c. more strong sulfuric acid in the flask and heat at boiling temperature for 15 minutes, cool, add

30 c.c. of water, boil, cool and filter through the same Gooch as before. Wash all the lead sulfate out of the flask into the Gooch crucible, wash the crucible and sulfate five times with small amounts of water, and carefully ignite the crucible. To do this place the crucible inside a larger one and heat the outside one to a dull red for 10 minutes, or, better, heat in a dull red hot muffle. Cool and weigh. The weight of the lead sulfate multiplied by 0.683 gives the weight of the lead.

If arsenic is present proceed as directed on page 234; if not, proceed as directed below.

Antimony.—Heat the filtrate, which should be less than 150 c.c. in volume, to 60°C. and titrate with standard permanganate solution. Run in the permanganate until the pink color, which quickly appears and does not fade, becomes a deep permanganate color. Agitate the solution a minute and then titrate the excess permanganate by standard ferrous sulfate solution. The $KMnO_4$ should be standardized against pure antimony treated in the same way. The iron value of the permanganate used minus the iron value of the ferrous sulfate used multiplied by 1.076 theoretically equals the antimony present. That is, a permanganate solution, 1 c.c. of which equals 0.010 gram of iron, equals 0.01076 gram theoretically of antimony. The end point is sharp and the results exact. It is not necessary or desirable to have HCl present.

Copper.—Now add 3 grams of tartaric acid to the solution and then NH_4OH until the solution is slightly alkaline, then add 2 c.c. of sulfuric acid and heat almost to boiling. Add 2 grams of Na_2SO_3 and when all is dissolved add a gram of KCNS dissolved in 10 c.c. of water. Shake the flask well and allow the precipitate to settle for 15 minutes while the solution is kept hot. Filter through an asbestos mat, wash well with water and then pour through the filter 40 c.c. of 10 per cent. NaOH, catching the solution in a clean beaker or flask. Wash the filter well with water and titrate the sulfocyanate as directed on page 211, for the analysis of copper ores.

Tin.—At the same time that the above analyses are being made, carry through another sample up to or through the titration for antimony, thus getting checks on the lead and antimony results. Then add to the solution one-third its volume of strong

HCl, transfer the solution to a 500 c.c. flask and stopper the flask with a three-hole stopper. Through one hole pass a glass tube which extends to the bottom of the flask. Through another pass an iron rod, the end in the flask being bent into a coil.

Add to the solution 5 c.c. of sulfuric acid containing 0.15 gram of antimony unless the sample contains a sufficient amount already. Heat to boiling and pass a stream of CO_2 or natural gas freed from H_2S by NaOH, through the solution by means of the glass tube. Continue the boiling (and current of gas) for 20 minutes after the solution becomes colorless. Cool the solution under a jet of water without stopping the current of gas, which should pass through rapidly while the flask is cooling to prevent the air from being drawn in. When cool, run in through the vacant hole 100 c.c. of distilled water, 3 c.c. of starch solution, draw up the iron rod, and titrate the tin with a N/10 solution of iodine. The blue end point fades after about a minute.

Modification when Arsenic is Present

If the metal contains arsenic the above process must be modified because arsenic interferes with the determination of antimony.

Process of Analysis.—Evaporate the filtrate from the lead sulfate until fumes of sulfuric acid appear, cool, add 15 c.c. of water, 35 c.c. of HCl, sp. gr. 1.20, and insert in the flask a clean rubber stopper, carrying a centigrade thermometer and a delivery tube. The thermometer should be about 1 in. from the surface of the liquid, so as to get the vapor temperature only, which should not go above 108°C. Connect the delivery tube to a figure S condenser which has one of its curves nearly filled with water and submerged in cold water in a 500 c.c. beaker, and its other free end dipping into about 75 c.c. of water in a 300 c.c. beaker.

The S condenser is about 18 in. long and $\frac{1}{2}$ in. inside diameter but tapers to about $\frac{1}{4}$ in. at the upper, and $\frac{1}{8}$ in. at the lower end to facilitate washing and to make the bubbles of gas small as they emerge into the beaker. This makes a perfect condensing apparatus in this case; it is very simple, easy to handle, has only one rubber connection besides the rubber stopper, and no cocks or

corks that leak. Nothing is lost through it except air from the flask at the very start.

Distill from 10 to 15 minutes, boiling gently, and keeping the vapor temperature at 107° for at least five minutes. The arsenic, as $AsCl_3$, is all distilled over even if the alloy contains 5 per cent., which is rare.

Arsenic.—Wash out the condenser into the 300 c.c. beaker, and add an excess of about 2 grams sodium bicarbonate to this solution which should now have a volume of about 200 c.c., and warm to a temperature of about 27°C. Titrate with standard iodine solution (page 225) and starch to a deep blue, which color will take 0.2 c.c. of iodine solution in a blank under the conditions used.

Antimony.—Cool the solution left in the flask, add about 130 c.c. of cold water and titrate with standard permanganate solution. The blank is 0.1 c.c. About 4 c.c. of hydrochloric acid must be present during this titration; usually enough is left in the flask from the distillation.

Tin.—Determine the tin as directed above.

Notes on the Process.—Arsenic consumes close to 1.5 times as much permanganate solution as antimony does. Hence, if the arsenic is not removed before the antimony determination, the results will be worthless. Most all alloys which contain antimony contain arsenic. The arsenic should be removed before the tin determination since it often causes high results in this case too.

Copper has no effect whatever on the antimony determination but when it exceeds about 3 per cent. it is apt to interfere with the tin determination. The amount of iron found in alloys is usually entirely oxidized in the concentrated sulfuric acid to the ferric state so that it does not interfere. There are no other common metals that interfere.

About the only causes of error in this method are too great a variation of the conditions stated and the use of impure chemicals.

For the reactions and remarks for the copper titration see page 210. For those for the tin titration see page 219. For the arsenic titration see page 174.

When the alloy containing antimony is dissolved in strong hot sulfuric acid the antimony goes into solution as $Sb_2(SO_4)_3$. This is titrated by the permanganate, thus,

$$5Sb_2(SO_4)_3+4KMnO_4+24H_2O=$$
$$10H_3SbO_4+2K_2SO_4+4MnSO_4+9H_2SO_4.$$

It is not best to have hydrochloric acid present when the antimony is titrated as the end point is so transient.

When the antimony is being titrated the solution will become pink long before the end point is reached, in fact the pink appears soon after the titration is started. The permanganate must be added until the solution becomes a deep permanganate color and the excess is then titrated with ferrous sulfate. If the solution contains 20 per cent. HCl the pink color does not appear before the end point is reached but the end color is evanescent.

References:

Demorest, *J. Ind. Eng. Chem.*, V, 842.

Stief, *J. Ind. Eng. Chem.*, VII, 211.

References on Other Methods:

Low, "Technical Methods of Ore Analysis," p. 333.

Price and Mead, "Technical Methods of Brass Analysis," pp. 157, 164.

McCay, *J. Am. Chem. Soc.*, XXXI, 373. Separation of Sn and Sb.

Dinam, *Mon. Sci.*, XXII, 600.

Kietreiber, *Osterr. Chem. Ztg.*, XIII, 146.

Goodwin, *J. Ind. Eng. Chem.*, III, 34.

Kopenhague, *Ann. chim. Anal.*, XVII, 241.

McCay, *J. Am. Chem. Soc.*, XXXII, 1241.

CHAPTER XXVIII

THE ANALYSIS OF SPELTER

Process of Analysis.—Dissolve 10 grams of sample in dilute nitric acid, boil, allow to settle, filter, wash, dry and ignite the precipitate as SnO_2. Generally there is no tin in the zinc and the solution is not filtered.

Dilute to 250 c.c., add enough nitric acid to have 15 per cent. present and electrolyze at a temperature of 50°C. and a current of 2 amperes, using preferably a gauze anode. The lead is all deposited in about a half hour. Dip the anode quickly in a beaker of pure water, then wash with alcohol, dry for 15 minutes at 230°C. and weigh. The precipitate of PbO_2 contains when dried in this way 86.43 per cent. Pb.

Iron.—Weigh 5 grams of sample and put in a 150 c.c. flask. Add 20 c.c. of water and 10 c.c. of hydrochloric acid and heat. When the action slows down add 30 c.c. of 1:3 sulfuric acid. When the zinc is all dissolved fill the flask to the neck with distilled water and filter quickly through a thin paper or pulp. The residue on the paper consists chiefly of lead. Dilute the filtrate to 400 c.c. and titrate the iron with permanganate of about N/20 strength.

When the sample is dissolved the iron goes in solution as ferrous iron. For absolutely accurate results the titrated solution should be again reduced, this time with H_2S, the excess H_2S boiled off while a current of CO_2 passes through, the solution cooled and titrated.

Cadmium.—Dissolve 20 grams of the sample in dilute hydrochloric acid sufficient to dissolve all the zinc except about a half gram. Filter off the residue of zinc, lead and cadmium and wash two times. Dissolve the residue in a little nitric acid, add 1 c.c. of sulfuric acid and evaporate to fumes. Add 20 c.c. of water, heat to dissolve all cadmium sulfate and filter off the lead sulfate. Make the filtrate alkaline with NH_4OH in excess, boil and filter

off any bismuth. Make the filtrate slightly acid with sulfuric acid and precipitate the cadmium with H_2S from the hot solution. Filter and wash a few times with H_2S water. Wash the precipitate back into the beaker, add a little KCN and shake until any copper sulfide is dissolved. Filter and wash well (on a small paper) with H_2S water.

Dissolve the sulfide in hot 1:1 HCl catching the solution in a weighed porcelain crucible. Add a few drops of sulfuric acid and evaporate to dryness, finally drive off the sulfuric acid at as low a heat as possible. Weigh and multiply the weight of the cadmium sulfate by 0.5390 to get the weight of cadmium.

References:
Berringer, "A text-book of Assaying," p. 268.
Price and Mead, "Technical Brass Analysis," p. 205.
Ericson, *Chem. Abs.*, VI, p. 3249.
Fairlie, *Metal. Ind.*, VIII, 386.

The following method for spelter analysis is recommended by Ericson (J. Ind. Eng. Chem., V, 401). Dissolve 19.2 grams of the sample in 200 c.c. of water and 43 c.c. of concentrated HCl, sp. gr. 1.2. Allow to stand over night, filter off the residue of lead, cadmium, and undissolved zinc, and wash with hot water. Transfer the residue back to the beaker with a jet of water, add 10 c.c. of strong HNO_3 and boil until brown fumes cease to come off. Filter, if traces of antimony or tin make the solution turbid. Add 75 c.c. of water, 30 c.c. of NH_4OH, and 5 to 10 grams of ammonium persulfate. Boil for five minutes and let the PbO_2 settle for 10 minutes. While still warm, filter through double filter paper and wash four times with a hot 10 per cent. NH_4OH solution and then five times with hot water. Transfer the precipitate back into the beaker, add 25 c.c. of hydrogen peroxide solution (20 c.c. of U. S. P. H_2O_2 in a liter of water plus 50 c.c. concentrated HNO_3). Stir until the PbO_2 is dissolved, add 15 c.c. of nitric acid, sp. gr. 1.2, and 100 c.c. of distilled water, and titrate the excess of H_2O_2 with standard permanganate, containing 0.568 gram of permanganate to the liter. Then the permanganate equal to the H_2O_2 solution used minus the permanganate required in the titration equals the lead in the sample in hundredths per cent. That is, if the H_2O_2 is equal to 70 c.c., and

30 c.c. of permanganate are used in the titration, the lead equals 0.40 per cent. of the sample. The reactions are

$$PbO_2+H_2O_2+2HNO_3=Pb(NO_3)_2+2H_2O+O_2$$
$$5H_2O_2+2KMnO_4+6HNO_3=2KNO_3+2Mn(NO_3)_2+8H_2O+5O_2$$

Hence $2KMnO_4=5Pb=10Fe$ and theoretically $\frac{5Pb}{10Fe}=1.851$, but actually the ratio is found to be 1.92.

In the filtrate from the PbO_2 the cadmium is determined as follows: boil the solution until nearly neutral and a white precipitate forms, take off the hot plate and add 40 c.c. of 1:3 sulfuric acid. Boil 10 minutes, dilute to 200 c.c. and precipitate the cadmium with H_2S. Filter through double filter paper and wash a few times. Dissolve the precipitate in as little warm dilute HCl as possible and wash with warm water. If copper is present it remains insoluble.

Nearly neutralize the filtrate with NH_4OH, add 8 grams of trichloracetic acid, dilute to 200 c.c. and precipitate the cadmium with H_2S. Filter off the CdS and determine it as above directed.

CHAPTER XXIX

BRASS AND BRONZE ANALYSIS

Brass is essentially an alloy of copper and zinc and bronze an alloy of copper and tin, but brass may have small amounts of lead and tin and other elements and bronze may have small amounts of lead and zinc and other elements.

Analysis of Brass.—Dissolve 1 gram of the drillings with a mixture of 5 c.c. of water and 10 c.c. of nitric acid. Cover with a glass and heat to boiling. When all red fumes are gone dilute to 75 c.c. and filter through a paper onto which has been sucked macerated filter paper by means of a suction filter arrangement. Wash well and if accurate results are not desired ignite the precipitate in a porcelain crucible and weigh as SnO_2 containing 78.8 per cent. tin. Since the SnO_2 is contaminated with all the phosphorus in the sample and with more or less copper and lead if present, it must be purified if accurate results are required. To do this, peel the mat of macerated paper and the precipitate of metastannic acid off of the filter paper, put it in the beaker in which the sample was dissolved and add 25 c.c. of NH_4HS made by saturating ammonia with H_2S. Heat until all the precipitate is dissolved except the small amount of sulfides of copper and lead, etc. Filter through the same paper as before and wash well with dilute NH_4HS water and electrolyze the filtrate after adding 4 grams of KCN and diluting to 150 c.c. Use a gauze cathode and a current of about 3 amperes. The KCN keeps sulfur from separating on the anode. The tin will all be deposited in 30 to 60 minutes. If the chemist prefers, he may determine the tin in the precipitate of metastannic acid by treating it, paper and all, exactly as described for tin in bearing metals on page 233.

To the filtrate from the metastannic acid, to which is added the sulfides obtained from the treatment of the metastannic acid with NH_4HS, add 5 c.c. of sulfuric acid and evaporate to fumes. Add 50 c.c. of water, heat until all copper sulfate is dissolved,

cool, filter and wash the lead sulfate with cold dilute sulfuric acid. The filter should be a Gooch crucible with asbestos mat. Ignite and weigh as directed on page 233.

Electrolyze the filtrate from the lead sulfate for copper after adding 5 c.c. of HNO_3, and after the copper is all out determine iron and zinc by precipitating the iron by NH_4OH and the zinc by Waring's method, as given on page 196.

If the sample does not contain tin, the solution is evaporated with sulfuric acid to fumes and the analysis carried on as given above after the evaporation with sulfuric acid.

If the brass does not contain tin and not much manganese, dissolve 1 gram in 20 c.c. of nitric acid, and dilute to 100 c.c. and electrolyze (using gauze cathode and anode) until the lead is deposited as PbO_2, then add 10 c.c. of NH_4OH and complete the deposition of the copper.

Solder Analysis.—Solders are composed of about half and half lead and tin and may be correctly analyzed either as directed above for brass, or, even better, as directed for the analysis of bearing metals.

Bronze Analysis.—Bronzes should be analyzed as directed for the analysis of brass, always dissolving the metastannic acid in NH_4HS and precipitating the tin electrolytically. The metastannic acid may be treated as directed under bearing metal analysis for tin.

References:

Demorest, *J. Ind. Eng. Chem.*, March, 1910.

Price and Mead, "Technical Analysis of Brass," p. 180.

CHAPTER XXX

THE ANALYSIS OF COAL AND COKE

In the laboratory examination of coal the points to be investigated are usually: First, the amount of moisture that it contains as it occurs in the mine or on the market. Second, the amount of the impurities present that affect its use, such as ash, sulfur, and phosphorus. Third, the amount and quality of the coke that it will produce. Fourth, the improvement that it undergoes by "washing." Fifth, the fuel value, including the calorific power and the evaporating power.

The sampling of coal is always a matter of considerable difficulty, as it deals with a mechanical mixture of several minerals which differ greatly in specific gravity; namely, pure coal, slate, bone coal and iron pyrite. These constituent minerals may occur in all degrees of size; for instance, the pyrite may be present as barely visible grains scattered all through the coal or as large lumps and streaks. It is obvious that in the latter case the difficulty of securing a small sample which shall contain the same percentage of the heavy pyrite as does the mass from which it is drawn is formidable. See page 6.

Finely crushed coal is liable to oxidation and change of composition on standing exposed to air at ordinary temperatures. Hence the analysis should be made soon after the final sampling.

The laboratory processes in use for coal testing comprise the "proximate" analysis, the ultimate analysis, the determination of sulfur and phosphorus, tests of the coking power, washing the coal, and finally the determination of the heating power either by calculation from the results of the ultimate analysis, or by use of the calorimeter.

Proximate Analysis

The method for proximate analysis here used is as given by Professor E. E. Somermeier of the Department of Metallurgy, Ohio State University, in his book, "Coal."

This analysis gives the composition of the coal under four headings as follows: moisture, volatile matter, fixed carbon, and ash.

The results obtained are more or less dependent upon the exact process used and small variations in working out the details of the process may

make a considerable difference in the results actually obtained, while a distinctly different process gives radically different values for some of the determinations. Hence the results are relative and not absolute and should be so regarded both by the chemist and by the user of the coal. The efforts of some chemists to find a method of determining the "true moisture" in coal might better be spent in trying to simplify and improve the method already in use for obtaining the comparative value.

Moisture.—The term moisture includes only the more or less loosely held water which is driven off by heating 1 gram of the finely ground sample for one hour at 105°C. A finely ground sample of coal during the operation undergoes changes due to oxidation and escape of gases, hence the actual value obtained for moisture is the amount of water driven off plus or minus any oxidation changes. In most coals if not ground excessively fine these oxidation changes are of minor importance compared to the moisture loss so that the reporting of this net loss as moisture does not lead to any serious errors, although it practically never represents the exact amount of water expelled. A sample of coal which has been heated for one hour at 105° will give off more moisture and undergo further oxidation changes if heated to a still higher temperature, the amount of moisture given off depending upon the kind of coal and upon the increase in temperature. The extent of the oxidation also increases with the temperature and varies with the kind of coal and fineness of the sample. While it is true that the results for moisture obtained by heating the sample to 105° have no absolute value but merely a relative one, it is equally true that when two samples of approximately the same kind of coal are treated in the same way for moisture by heating to 105°, the difference in the results obtained show very closely the difference in the amount of loosely held moisture in the coal. Usually this is what the user of the coal wishes to know and on this account the moisture determination has importance and value.

Volatile Matter.—The determination of volatile matter is an arbitrary one and the results are obtained by following a certain prescribed procedure, which is essentially to heat 1 gram of the finely ground sample in a covered platinum crucible over the full flame of a Bunsen burner for seven minutes. The loss in weight represents moisture plus volatile matter. Subtracting the value for moisture from this result gives the amount of volatile matter in the coal.

This determination cannot be regarded as entirely satisfactory as the result obtained is to a considerable degree dependent upon the particular conditions under which the sample was run and two different chemists in two different laboratories both trying to follow out the same method of procedure may easily obtain results for volatile matter upon the same sample of coal which may differ by 2 or 3 per cent. Further-

more, some high-moisture coals suffer mechanical losses during the heating to drive off the volatile matter. Such samples require special treatment to insure results of even approximate accuracy. On account of such possible differences and errors this determination cannot be regarded as very exact. It is, however, true that the same chemist working in the same way with the same crucibles, the same height of gas flame, the same Bunsen burner, etc., can obtain results which will duplicate within a few tenths of 1 per cent. and in control work the same chemist's results on approximately the same coals ought to be comparable among themselves to within less than 1 per cent. The amount of volatile matter in itself gives very little idea of the coal, as two coals with approximately the same amount of volatile matter may differ very greatly in heating value, physical properties, etc., and any significance which the determination of volatile matter actually has is largely a relative one which may be of value when the same or similar coals are compared with one another.

The volatile matter consists essentially of any combined water in the coal plus a portion of the sulfur, on an average probably about one-half of the total sulfur present in the coal, plus the nitrogen in the coal, plus hydrocarbons of unknown and varying composition. The nitrogen and combined water in the volatile matter have no heating value and, if present in large amounts, the heating value of the combustible will be correspondingly lower.

Fixed Carbon.—Fixed carbon represents the difference obtained by subtracting the percentage of moisture, volatile matter and ash from 100. The fixed carbon as its name indicates is mostly carbon. Approximately one-half the sulfur in the coal present in the form of pyrite and a variable portion of that present as organic sulfur remains with the fixed carbon and the heating value of the fixed carbon is, on this account, somewhat lower than that of pure carbon. On the other hand, small amounts of hydrogen may be retained in the fixed carbon which would slightly increase its heating value. In most coals the heating value per unit of the fixed carbon is not far from that of carbon —8080 calories—and this value may be used in estimating heat values without any great error. With high sulfur coals, a somewhat lower value, approximately 30 calories lower for each per cent. of sulfur in the coal, is probably more nearly a correct value. This is based on the assumption that one-half of the sulfur remains with the fixed carbon and that not more than traces of hydrogen are retained in the fixed carbon.

Ash.—As ordinarily reported, this is the weight of ignited mineral matter in the coal. It is not the same as the inorganic mineral matter of the coal, for clay loses water on heating, sulfides are oxidized and carbonates are calcined.

Methods of Analysis

The samples from the sampling room or laboratory should be sent to the chemical laboratory in wide-mouth bottles securely closed with rubber stoppers. Ordinary 4 oz. wide-mouth bottles are very convenient for coal samples.

Weighing Out a Sample for a Determination.—In weighing out portions of the laboratory sample for a determination, the sample should be well mixed. An efficient method of mixing is as follows: The material is thoroughly mixed by giving the bottle 15 to 20 rotations with an up-ending and tilting movement of the bottle to insure mixing of the top and bottom portions of the sample. For satisfactory mixing in this way the sample should not fill the bottle more than half full. After the mixing in the bottle the stopper is removed and the sample still further mixed by means of a sampling spoon, and successive small portions taken until the amount required for the determination is secured, especial care being taken to again securely stopper the bottle before setting it aside for other determinations. If the sample more than half fills the bottle it should be emptied out on paper, well mixed and a sufficient amount discarded until the remainder is small enough to be properly handled in the sampling bottle.

Moisture.—A 1 gram portion of the well-mixed 60-mesh sample is weighed into an empty capsule or crucible and heated for an hour at 105°C. in a constant-temperature oven. The capsule is then removed from the oven, covered and cooled in a desiccator over sulfuric acid.

The loss in weight times 100 is considered as the percentage of moisture. The writer prefers, for moisture determinations, porcelain capsules about 1 in. high by 1⅝ in. in diameter at the top. The particular kind used has been obtained from The Henry Heil Chemical Co., of St. Louis, and are designated as porcelain moisture-capsules No. 2. They are much more substantial and satisfactory than the ordinary porcelain crucible.

The lids used in connection with the capsules are stamped from sheet aluminium. They are light and unbreakable and much more convenient to handle than the ordinary covers used with porcelain crucibles. In weighing out the sample at the beginning of the determination the lid

is placed upon the balance pan under the empty capsule in which the sample is weighed.

The oven used for a number of years in this laboratory is a double-walled copper cylinder, see Fig. 14; the space between the outer and inner walls being filled with a solution of glycerine in water, the proportions being so adjusted that the boiling solution maintains a temperature of 105°C. in the inner chamber of the oven. The inner cylinder is 4½ in. in diameter by 7 in. long. A removable perforated shelf fits into this inner cylinder, the perforations holding six capsules.

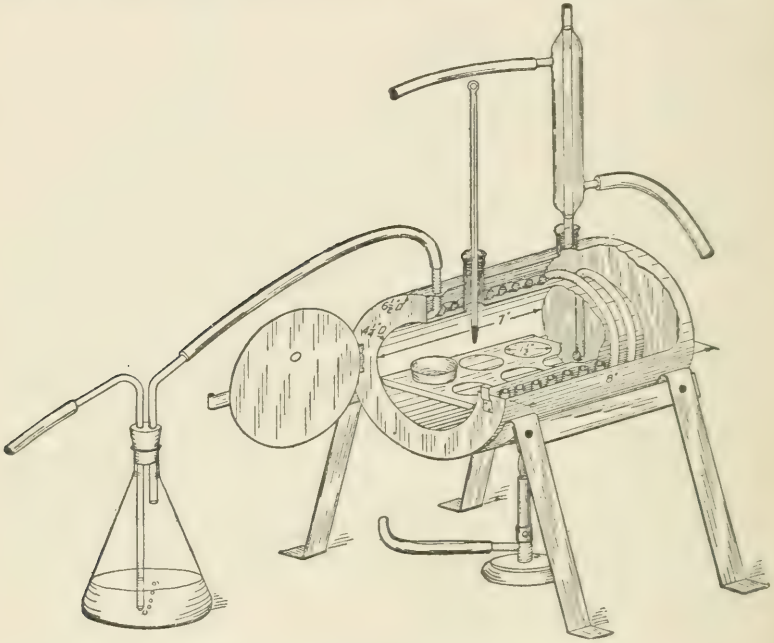

Fig. 14.

The outer cylinder is 6½ in. in diameter by 8 in. long. Concentration of the solution is prevented by means of a condenser fitted onto the top of the outer cylinder. Air is admitted into the inner chamber of the oven through a coil of block tin or copper tubing, which passes around the inner cylinder and is surrounded by the glycerine solution. The inner end of this tubing is soldered into the rear wall of the inner chamber; the outer end is connected to a flask containing concentrated sulfuric acid. During a determination a current of air dried by passing through the sulfuric acid is passed through the copper or tin tube into

the inner chamber of the oven. Passing over the samples it takes up the moisture and escapes through a small opening in the top of the door of the oven. The air is passed through at such a rate that a volume equal to the capacity of the oven passes through every six or eight minutes. Operating a moisture oven in this way insures a uniform condition in the oven irrespective of laboratory humidity and temperature conditions, and results run at different times are strictly comparable, which is not the case in an ordinary moisture oven.

The cut shows nine turns of tubing; however, four or five turns are probably just as efficient and are less expensive.

The use of sulfuric acid in the desiccator in which the moisture sample is cooled gives more concordant results than where calcium chloride is used. Experiments show that if the dry sample is allowed to remain over calcium chloride for any considerable period of time it increases in weight and the results for moisture are accordingly low. To avoid the danger of sulfuric acid, in the desiccator, splashing up on the bottom of the capsule when the desiccator is carried around the laboratory, a thin sheet of asbestos paper should be placed below the capsule, care being taken to have it fit loosely enough in the desiccator to allow free circulation of air.

Ash.—The ash is determined in the residue of coal from the moisture determination. The capsule containing the coal is placed in a muffle furnace and slowly heated until the volatile matter is given off. This slow heating avoids coking the sample and renders it easier to burn to ash. After the volatile matter is expelled, the temperature of the muffle is raised to redness and the heating is continued until all black carbon is burned out. The capsule is then removed from the muffle furnace, cooled in a desiccator and weighed. It is then replaced in the muffle, for 30 minutes, again cooled and re-weighed. If the change in weight is less than 0.0005 gram the ash is considered burned to constant weight. If the variation is greater than this, the ash is again ignited for 30 minutes and again cooled and re-weighed, the process being continued until the difference in weight between two successive ignitions is less than 0.0005 gram. In the case of coals high in iron, ignition to constant weight is sometimes difficult on account of small variations in weight due to oxidation and reduction of the compounds of iron. The amount of ash as determined represents the ignited mineral matter in the coal.

In regular routine work the cooling in desiccators may be dispensed with and the capsules cooled on clay triangles in the open air. A set of six triangles mounted on a wood base is very convenient for carrying the capsules from the furnace to the balance and from the balance back to the furnace. This arrangement is lighter and easier to handle than desiccators and the time required for cooling is much less.

The capsules cooled in air weigh about 0.0005 gram more than if cooled in desiccators, hence the ash results run a trifle high, but for most samples the difference is of very minor importance and the saving in time and labor considerable. If results of highest accuracy are required the cooling should be done in desiccators.

Volatile Matter—A 1-gram sample of the fine (60-mesh) coal is weighed into a bright, well-burnished 20-gram platinum crucible with a close-fitting cover. The crucible and contents are heated upon a platinum or nichrome triangle for seven minutes over a Meker flame not less than 15 cm. high.

The crucible and residue are cooled and weighed, the loss in weight minus the weight of the moisture in the sample determined at 105°C., times 100 equals the percentage of volatile matter.

To protect the crucible from air currents it is desirable to enclose the flame in a chimney. A cylindrical chimney 15 cm. long by 7 cm. in diameter, notched at the top so that the platinum triangle is about 3 cm. below the top of the chimney, makes a satisfactory working arrangement.

This chimney is preferably of sheet-iron lined with asbestos but a fairly satisfactory chimney can be made by moistening a thick sheet of asbestos and rolling it into a cylinder. This, if well wrapped with wire, makes a fairly serviceable chimney. For lignites and coals containing a high percentage of moisture, the method should be modified by giving the sample a preliminary heating at a low temperature for several minutes to drive out the moisture, in order to avoid mechanical losses which will occur if such a sample is heated over the full flame of the burner from the beginning. This preliminary heating for three to four minutes should be followed by the regular seven-minute application of the full flame, after which the sample is cooled and weighed as in the regular determination.

The higher the temperature at which the volatile matter is expelled the greater is the percentage of volatile matter obtained. The latest

data on this subject (Sept., 1912) is by Fieldner and Hall.[1] As a result of their experiments they recommend 1000°C. as the most desirable temperature at which to make this determination. Their results using a No. 4 Meker burner with natural gas compare very favorably with their results obtained by heating the sample in an electric furnace. The crucible should be at least hot enough to melt pure K_2CrO_4 (melting-point 940°C.).

Fixed Carbon.—The fixed carbon is the difference between 100 and the sum of the moisture, ash and volatile matter.

The Determination of Sulfur in Coal. Eschka's Method.—Sulfur exists in coal in three forms: Pyrite, "organic sulfur," and sulfates. By heating coal with a mixture of MgO and Na_2CO_3, and with ample access of air, all unoxidized sulfur is converted to sulfites and sulfates of soda and magnesia. On boiling the burned mass with water, these, as well as any sulfuric acid existing previously in the coal as sulfate, are all dissolved out as alkaline salts. By adding bromine water to the solution the sulfites are oxidized to sulfates, and then the total sulfur can be estimated as $BaSO_4$, by precipitation with $BaCl_2$.

Preparation of the Soda-magnesia Mixture (Eschka Mixture).—Procure a "light" calcined magnesium oxide, which must be free from sulfur and water. If it contains moisture, ignite it at a dull red heat in a covered platinum crucible. The heavy dense oxide is not satisfactory.

Mix two parts of the MgO with one part by weight of pure Na_2CO_3 previously dried at a dull-red heat. Grind the two together until thoroughly mixed, and keep the mixture in a glass-stoppered bottle.

If a satisfactory sample of sulfur-free MgO is not available, it may be prepared as follows:

Take a good quality of commercial "light calcined magnesia;" add about 2 per cent. of c.p. sodium carbonate, and then stir it up in enough boiling water to make a thin liquid. Boil the mixture a few minutes and let settle; decant off the liquid by a siphon. Add water, stir up, settle, and again decant. Continue this washing by decantation until a portion of the liquid, after being acidified with HCl, shows no trace of sulfates when tested with $BaCl_2$. Now pour the MgO onto a large filter, let it drain and air dry. It is now free from sulfur compounds. Ignite the air dried MgO in a covered platinum crucible until all water is expelled.

A clean tin bucket can be used in this process where a quantity is to be prepared.

[1] Eighth International Congress of Applied Chemistry, X, p. 139.

Process of Analysis.—Weigh 1 gram of the coal or coke (which must be finely powdered, especially in the case of coke), then weigh or measure out roughly 2 grams of the "Eschka mixture." Put about two-thirds of this into a 30 c.c. platinum crucible. Add the weighed coal and stir the mixture in the crucible thoroughly with a small platinum spatula or glass rod, and then settle it down by tapping the crucible on the table. Now cover the contents of the crucible with the remaining portion of the "Eschka mixture." Set the crucible, in an inclined position, over a small alcohol or sulfur-free natural-gas flame, so that the tip of the flame may barely touch the crucible near the *top of the mixture.* The heat must be carefully regulated, so that no blackening of the white cover layer takes place, and no trace of smoke appears. The cover should be laid against the mouth of the crucible to assist the draught. The mixture soon ignites and will gradually burn through, as may be observed through fissures which open in the mass. The coal will usually burn completely in less than an hour. The heat may be raised toward the end of the combustion and the lamp set back under the bottom of the crucible. A higher heat may be used with cokes from the start; as these give no volatile products and burn slowly. Stir up the powder occasionally with a hot glass rod or platinum wire. When the burning is complete, all trace of the black coal will have disappeared and only a light, reddish-gray mass remain. Cool and then pour the powder into a 200 c.c. beaker. Add about 75 c.c. of boiling water, stir and digest on a water-bath. Then filter, washing the residue twice by adding about 30 c.c. of hot water, and decanting off, then transfer to the filter. Wash on the filter until the volume of the filtrate amounts to about 200 c.c. This will extract practically all of the sulfur.

Add bromine water to the filtrate until the liquid is colored yellow; then add 3 c.c. of HCl and warm until the CO_2 is expelled. Test the solution with litmus paper to make sure that it is distinctly acid. Then add 10 c.c. of $BaCl_2$ solution (10 per cent.). Set the beaker on a warm plate, but do not let it come to boiling. Stir the liquid occasionally until the $BaSO_4$ becomes granular and settles well. Now filter, wash, dry, ignite and weigh the $BaSO_4$. Calculate the sulfur as S.

Always examine the *residue* which was extracted with water, by washing it off the filter into a beaker, and then adding a little HCl and warming. All will dissolve but a little ash. If more than a trace of *unburned* coal is seen in the residue, the analysis must be repeated.

The residue sometimes retains a very small trace of sulfur. To test it, add a little bromine water with the HCl as above and boil. Filter off the liquid and add $BaCl_2$. If any sulfur is found, add it to the main precipitate.

Notes on the Process.—This is one of the best methods for the determination of sulfur in coals. If care be taken in all details, especially as to rate of heating, there is no loss of sulfur whatever.

It has been proposed to substitute K_2CO_3 for the Na_2CO_3, the claim being made that there is less danger of loss of S with the potassium carbonate, but experience has shown it to be absolutely unnecessary.

The use of alcohol or sulfur-free natural gas as a source of heat is *essential.* All coal gas contains sufficient sulfur to *vitiate* the results.

The most difficult step in the process is the burning out. In analyzing coke much time can be saved by using a higher heat than is given by an alcohol lamp. This can be obtained by using a gasoline blast lamp or working in a muffle heated by gasoline. If the muffle is heated by coke or coal gas, care must be taken that no sulfur gets into it from the fuel.

Determinations of ash in coal and coke must not be made in the muffle at the same time with sulfur determinations; as the SO_2 formed will be absorbed by the "Eschka mixture" and makes the results high.

Cokes can be burned with "Eschka mixture" in a platinum dish. They should be stirred frequently, which will hasten the combustion. It is unsafe to treat coals high in volatile matter in this way; because the gas given off must be burned in the mixture and not on the surface, or sulfur may escape. They must be burned in the crucible, and by properly regulating the air supply and the temperature the gas can be rapidly burned as it is given off. When the volatile matter is expelled the heat can be raised and the mixture stirred.

A blank determination must be run on the reagents.

Sulfur in the Calorimeter Washings.—The determination of the sulfur in the washings from the calorimeter is as follows: The washings are slightly acidulated with hydrochloric acid and filtered from the residue of ash, the filtrate is heated to boiling and the sulfur precipitated as in the Eschka method.

References:

Eschka, *Z. Anal. Chem.*, XIII, p. 344.

Drown, *Trans.* Am. Inst. Mining Engrs., IX, p. 660.

The Determination of Phosphorus in Coal and Coke.—Ten grams of the coal are carefully burned to ash in a porcelain crucible. The ash is then analyzed for phosphorus exactly as though it were an iron ore, excepting that it is always necessary to fuse the insoluble portion. HCl will not dissolve all the phosphorus out of the ash even on prolonged boiling, though the amount left is usually very trifling.

Process of Analysis.—Mix the ash from 10 grams of the coal with six times its weight of pure Na_2CO_3 and half its weight of $NaNO_3$. Fuse the mixture in a platinum crucible, soften the fusion with water, dissolve in an excess of HCl, evaporate to dryness, take up with HCl and water, and filter from the SiO_2; then proceed as by the yellow precipitate method for phosphorus in iron ores (page 45 et seq.).

The fusion can be avoided by the use of hydrofluoric acid as follows: Add 5 c.c. of dilute HCl and 10 c.c. of HF to the ash in the platinum crucible. Evaporate to dryness in a good hood; do not bake the residue and thus render it insoluble. When cool, add 15 c.c. of dilute HCl and heat. The residue should dissolve completely, but a little insoluble matter may be filtered off and neglected. Put the solution into a flask, add NH_4OH, then HNO_3, then molybdic acid solution, and "shake down" the phosphorus as in the Emmerton method. The yellow precipitate may be either weighed or titrated.

Reference:

See J. M. Camp, *Iron Age*, LXV, p. 17. Also "Methods around Pittsburgh," p. 139.

The Ultimate Analysis of Coal

The Determination of the Carbon and Hydrogen by Combustion in Oxygen.—The coal, placed in a boat of porcelain or platinum, is burned in a combustion tube, through which a current of purified air and oxygen gas is passed. The H_2O and CO_2 produced are absorbed and weighed. As the coal contains sulfur, the gases produced by the combustion must be passed over lead chromate to absorb the SO_2 formed.

The same chromate can be used for many determinations. As long as it does not turn green for more than one-fifth of the length in the

tube it is perfectly safe. The writer has used the same chromate for over fifty combustions, and then tested it by burning sulfur in the tube, and found no SO_2 escaping the chromate.

The principal difficulty in the process arises from the fact that coal begins to decompose at a low temperature, giving off among other products methane, a gas which it is very difficult to burn completely, and which is very likely to escape from the combustion tube unoxidized. To secure its complete combustion a *long* and *hot* layer of copper oxide is necessary.

The process requires close attention to details and skill in fitting up and manipulating apparatus. The precautions mentioned under the combustion method for carbon apply equally here, especially as to the purity of the oxygen and the copper oxide. The latter should be examined for $CaCO_3$ or other carbonates which are liable to give up CO_2 on heating, and also for bases which may absorb CO_2. $CaCO_3$ will be decomposed at one temperature, and the CaO formed will absorb CO_2 at another. CuO can be examined for CaO by extracting it with a little dilute HNO_3, adding NH_4OH in excess, and then testing the liquid with $(NH)_4C_2O_4$. The "wire" oxide is the best and should be used.

The asbestos used in the tube must be freed from carbonates by treatment with HCl and ignition.

The oxygen must be tested as to its purity, and must not be kept in rubber bags or passed through long rubber tubes.

Oxygen can be purchased in cylinders, or it can be made by heating a mixture of pure $KClO_3$ with one-third of its weight of MnO_2 in a 250 c.c. round-bottomed, long-necked flask of hard glass (Kjeldahl flask). The flask should be surrounded by a cylinder of wire gauze to protect the face in case of an explosion. The mixture must be tested for carbon by first heating a little of it on a platinum crucible cover; it should not sparkle or flash. The gas so made will contain some chlorine and CO_2 which must be removed by KOH solution.

The Arrangement of the Apparatus.—This is in many respects similar to that used in the determination of the carbon in iron, except that as the water is to be weighed as well as the CO_2, tubes for absorbing it are added.

The train comprises: First, a gas holder for the oxygen. The one described on page 114 is very satisfactory. About 500 c.c. of oxygen is required for each combustion.

Where only an occasional combustion is made a simple gas holder can be made of a couple of glass bottles.

Second, the purifying train for the air and oxygen. This is made in duplicate, as described under the determination of carbon. The bottle containing sulfuric acid absorbs the traces of ammonia or its salts usually present in the air of a laboratory. If these were not taken out they would burn in the tube and form water and make the results on hydrogen too high. As it is as important to purify the air from moisture as from CO_2 in this process the train is made larger and separate U-tubes are used for the soda lime and the $CaCl_2$.

Fig. 15 shows the details: A is a bottle with moderately concentrated H_2SO_4; B is a bottle with about 50 c.c. of KOH solution of 1.27 sp. gr.; C is the U-tube with the soda lime, and D is the U-tube with the $CaCl_2$.

Third, the combustion tube: This should rest on asbestos in the trough of a long gas combustion furnace. The tube should

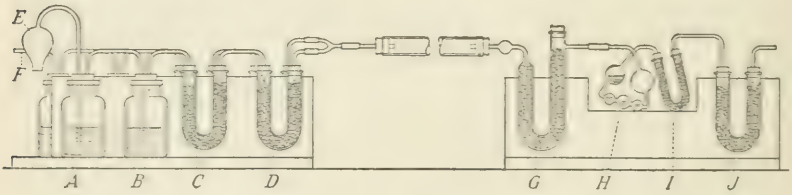

Fig. 15.

be made of the best infusible glass and have an internal diameter of about $\frac{1}{2}$ in. The walls of the tube must not be too thick or they will crack. The ends of the tube should be rounded by heating and should be fitted with good soft corks, well rolled. Rubber connections with this tube are not to be recommended, as they become warm and are liable to give off hydrocarbon vapor and to absorb some CO_2. A long tube and furnace are necessary. The writer uses a furnace with twenty-five burners and a tube 40 in. long.

The tube is filled as follows: A space of 5 to $5\frac{1}{2}$ in. is left empty at the end nearest the absorbing train. Then follows: 1. A plug of asbestos. 2. Five inches of fused $PbCrO_4$ in small lumps. 3. An asbestos plug. 4. Twelve to 14 in. of pure, recently ignited "wire" CuO (or a close coil of fine copper gauze thoroughly oxidized by heating it in a stream of pure oxygen).

5. An asbestos plug. 6. The "boat" for holding the coal. There must be 13 or 14 in. of empty tube following the last asbestos plug, so that the part of the tube in which the "boat" is placed will be well in the furnace, and yet the tube itself projects at least 4 in. outside of the furnace. The end of the tube is connected by a cork, glass tube, and rubber connection with the purifying train. The cork connections in the ends of the combustion tube must not become hot enough to run any risk of being burned; hence a sufficient length of tube must project from the furnace at each end. These projecting ends should be further protected from the heat of the furnace by discs of sheet asbestos 6 or 7 in. in diameter, with holes in the center through which the combustion tube passes.

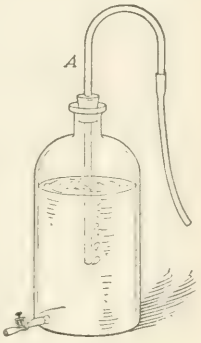

FIG. 16.

With a tube arranged as above it is not necessary to insert a copper coil behind the "boat," as is sometimes directed, provided the coal is slowly heated so as to expel the volatile matter gradually, and that a continuous current of air or oxygen is kept passing through the tube, so as to prevent the products of the decomposition from working back, condensing in the cool part of the tube, and so escaping combustion.

Fourth, is the absorbing train following the combustion tube, shown in Fig. 15, and consisting of G, a $CaCl_2$ tube, the end of which is inserted into the cork of the combustion tube; H, Liebig potash bulbs; I, a soda-lime-calcium chloride tube similar to that used in connection with the potash bulbs in the determination of carbon in iron; J, a guard tube similar to I but reversed, which is connected with an aspirator for drawing air through the apparatus.

A "Mariotte bottle," arranged as shown in Fig. 16, makes the best aspirator. The suction tube, A, passes in through a rubber stopper at the top and reaches nearly to the level of the run-out tube. By slipping the suction tube up or down, the suction head can be regulated so as to barely overcome the resistance of the train, and will then remain exactly the same as long as the water in the bottle is above the end of the tube, and thus the rate of aspiration can be more easily kept constant.

Testing the Apparatus.—First, see that it is perfectly tight by starting the aspirator and shutting off the entrance of air. Second, heat the tube red hot throughout and aspirate two liters. Detach and weigh the potash bulbs and U-tube. Connect up again and aspirate ½ liter of oxygen and then 2 liters of air. Detach the tubes and weigh. There should be neither gain nor loss of weight. When consecutive weighings are found to agree within 0.5 mg., the apparatus is ready for the analysis.

Process of Analysis.—Ignite and cool the boat. Weigh into it 0.2 gram of the finely pulverized and well-mixed coal. (The sample must be made *very fine*, lest by weighing so small a quantity average results will not be obtained.) Insert the boat into its proper place and connect up the apparatus. Then carefully heat the $PbCrO_4$ to *dull* redness and the CuO to bright redness, drawing a slow current of air through the apparatus all the time. Now heat the tube behind the coal and then the coal itself, cautiously, until the volatile products are slowly driven off and carried forward over the hot CuO. Then introduce oxygen, regulating the supply so as to avoid too vigorous combustion and consequent fusion of the ash, which will lead to retention of carbon. After the carbon is all burned, which is shown by the sudden disappearance of the glow, continue the oxygen for two minutes, then cut it off and aspirate air. Turn off the gas burners and let the tube cool. Continue the aspiration until 1200 c.c. or more (at least seven times the capacity of the tube and absorbing train) has been drawn through. Now detach the absorption train and weigh. The increase in the weight of the $CaCl_2$ tube gives the water produced. This divided by 9 gives the weight of the hydrogen in the coal. The increase in the CO_2 apparatus is the CO_2; three-elevenths of this is carbon. The apparatus is now ready for another determination, as the CuO will all have been reoxidized by the air current.

The aspiration should be so regulated that not more than two or three bubbles pass through the potash bulbs per second. During the combustion in the oxygen the gas will consist largely of CO_2 and will be almost wholly absorbed, though the flow of oxygen into the apparatus may be quite rapid at the time. Care must be taken that the oxygen supply is sufficient to prevent back suction at this time.

As soon as the CO_2 is absorbed the gas may begin to run through the potash bulbs too rapidly unless the gas supply is promptly reduced.

The pressure of the gas in the tube should be kept near that of the atmosphere. This can be accomplished by careful regulation of the gas and the aspirator.

As was noted in the determination of carbon in steel, it is desirable to reduce the necessary aspiration to as small a volume as possible by using small connection tubes and a compact train. This saves time and increases accuracy.

After the boat containing the ash is withdrawn from the tube, weigh it. The ash so determined should agree with that found in the proximate analysis.

The tube should be kept carefully closed with good corks when not in use. A train and tube such as that described can be used for months. A good tube of Jena glass, while it may twist out of shape badly, will not crack or blow if carefully handled. Fifty or more determinations can usually be made on one filling of the tube.

The Determination of the Nitrogen in Coal[1]

One gram of the very finely pulverized coal is boiled with 30 c.c. of concentrated H_2SO_4, 7 grams of K_2SO_4 and 0.5 gram of metallic mercury in a Kjeldahl flask until the carbon is completely oxidized and the liquid is nearly colorless. A little potassium permanganate is then added. When the liquid is cool it is largely diluted with water, the mercury precipitated by K_2S and the ammonia it contains determined by distillation after adding an excess of solution of NaOH with cochineal indicator. This is the "Kjeldahl process," and depends on the fact that all the nitrogen is converted into ammonia by the treatment with H_2SO_4. For a complete description of the process, see Report of the Proceedings of the Association of Official Agricultural Chemists, Bulletin of the U. S. Department of Agriculture, 1895, No. 46. The results on coal are accurate, provided the sample is very finely pulverized and time enough given in the digestion to entirely oxidize the coal. This may take two or three hours.

[1] Fieldner, *J. Ind. Eng. Chem.*, VII, 106.

The soda-lime method can also be used and will give satisfactory results, provided the coal is completely burned and the soda-lime heated in the tube until it shows no more black color and leaves no unburned carbon when tested by solution in HCl. For a description of this method, see Fresenius Quantitative Analysis.

The Oxygen In Coal

As no good method is known for the direct determination of the oxygen in coal, it is always determined by difference, the sum of the percentages of H, C, N, S, and ash being subtracted from 100 and the remainder called oxygen. The result so obtained is always inaccurate, the error increasing with the percentages of the ash and sulfur. The weight of the ash does not represent that of the mineral matter in the coal, the pyrite in the coal being burned to Fe_2O_3 and the sulfur passing off as SO_2. Thus 4 atoms of S in 2 FeS_2 is replaced by 3 atoms of O in the Fe_2O_3, and the loss of weight is equal to $\frac{5}{8}$ of the S. For this reason many chemists use $\frac{5}{8}$ S instead of S in the determination of O by difference. As coals contain sulfur in other forms than FeS_2, and also frequently other compounds that lose weight on burning, such as $FeCO_3$ and $CaCO_3$, it is doubtful whether the results obtained in this way are any better than those given by the simple formula first given.

Testing a Coal as to the Quality of the Coke

In order to obtain the analysis of the coke produced from a coal, it is necessary to prepare a sample of the coke. This can be done in a small wind furnace as follows: Select two clay crucibles of such a size that one will set easily inside of the other. The writer uses a Denver fire clay "20-gram assay" crucible for the inner and a large "Hessian" for the outer. Grind a cover onto the inner one with sand until it fits closely. Put the larger one in the furnace and let it get bright red hot. Meanwhile charge the smaller with 100 grams of the coal, crushed to about $\frac{1}{4}$ in. mesh. Cover the smaller crucible and set it in the large one, throw a little coal in on top of it, and then carefully cover the larger one. At the end of an hour take out both, put a little more coal into the outer crucible, and then let them cool while covered. When cool, take out the inner crucible and remove the coke from it. The object of the coal in the outer crucible is to prevent oxygen from getting into the coke and burning out sulfur.

The Determination of the Porosity of Coke

The value of coke as a blast-furnace fuel depends somewhat on its porosity, as its speed of combustion will increase with the surface exposed to the blast.

The porosity is usually expressed as the percentage that the volume of the pores forms of the volume of the coke.

It can be determined by weighing the coke in air and then in water, and then filling the pores with water and weighing it again.

The difficulty of filling the pores with water is, however, so great that the results are very uncertain. It requires long boiling in water and repeated exhaustions under an air pump to remove the air; and as there are probably pores that do not open to the surface, the filling is never complete.

The following method, depending on the determination of the true specific gravity of the coke substance and the measurement of the volume of the coke, is much preferable. It is essentially that published by W. C. Anderson, J. Soc. Chem. Ind., XV, p. 20.

Determination of the Specific Gravity of the Coke Substance.— Into the neck of a 50 cc. specific gravity bottle put a glass tube wide enough to fit air tight when surrounded with a collar made of a rubber tube. The glass tube must have a bulb about an inch in diameter blown in it just above the bottle. It serves to catch and return anything boiling out of the flask. Weigh into this bottle 3.5 grams of the pulverized coke. The coke must be ground in a Wedgewood mortar until it will go through a 40-mesh sieve, and dried at 100°C.

Now add about 20 c.c. of water to the bottle and set it on a water bath for 15 minutes, shaking it occasionally till the coke powder is saturated. Now attach to the tube a Bunsen suction pump giving a good vacuum and exhaust the air till the liquid boils gently. Continue the boiling in a vacuum for two and one-half hours. Remove the flask, cool it, fill it up with water, and weigh as usual after inserting the stopper.

The bottle should have a counterpoise, of course, so that the weight obtained will be that of the coke and the water only. As the bottle holds exactly 50 grams of water, the specific gravity of the coke will be:

$$\frac{W}{W - (W' - 50)}$$

in which W equals the weight of the coke, and W′ the weight of the coke and water together. The true specific gravity of coke taken in this way varies from 1.75 to 2.00.

The Determination of the Volume or Apparent Specific Gravity of the Coke in Lumps.—Several average lumps should be selected and broken up just enough to exclude any large mechanical fissures or cavities. They should then be brushed free from all dust and dirt and carefully dried and weighed. The volume of these fragments is then determined by measuring the amount of water they displace.

This can be done with sufficient accuracy in the following simple apparatus: Take a pint "ointment jar" with a wide mouth and a brass or aluminium screw cap. Cut a gasket of sheet rubber to fit over the end of the jar, so that the top will screw down onto it and make a tight joint. The end of the jar should be ground smooth. Cut a small hole in the top which should be just large enough to admit the stem of a 50 c.c. pipette. Screw on the top and fill the jar with water till it runs out of the top and includes no air bubbles. Carefully take out 50 or 100 c.c. of the water by means of a pipette put in through the hole in the top. Now unscrew the top, put in 50 or 100 grams of the weighed lumps of coke, shake them around to loosen air bubbles, replace the cap on the jar and run in water from a burette until the water comes exactly to the level of the hole. The difference between that measured out with the pipette and that measured back in with the burette, will be the volume of the coke in cubic centimeters.

To find the volume of the pores in the coke, subtract its weight divided by its true specific gravity from the volume of the coke as determined above. The percentage that the pores form of the total volume of the coke will be:

$$100\left(1 - \frac{\text{wt. of the coke}}{\text{vol. of coke} \times \text{sp. gr.}}\right)$$

Testing the Effect of "Washing" on Coal

The object of the washing of coal on jigs or other washers is the reduction of the ash and the sulfur in the coal. The benefit that a given coal will receive in the process will depend upon the form in which

these impurities occur in it. Only the ash that is due to intermixed slate and the sulfur that is in the form of free pyrite can be removed by the process, which depends upon the difference in the specific gravity between these materials and the coal. The fineness to which the coal must be crushed in order to effect a satisfactory breaking apart of the heavy and light material will depend upon the nature of the coal seam. The finer the coal has to be crushed the greater will be the loss of coal in the slimes. All these points can be investigated in the laboratory.

The operation consists in crushing the coal to some determined maximum size, then separating it into a series of sizes by sieves, and finally separating these sizes into their heavy and light components.

The specific gravity of coal is less than 1.35 while that of the impurities is always above this figure; hence the separation into light and heavy parts can be made, as suggested by Dr. Drown, by mixing the coal with a solution of $CaCl_2$, of 1.35 sp. gr., in which the coal will float and in which the impurities will sink.

The apparatus needed consists of, first, a set of sieves of $\frac{1}{2}$, $\frac{1}{4}$ and $\frac{1}{20}$ in. mesh; second, a "miner's pan" or some equivalent in which a small quantity of material can be washed; third, a solution of calcium chloride of 1.35 sp. gr., made by dissolving 1 lb. of crude $CaCl_2$ in a pint of water, and when the solution has cooled, diluting it to exactly the right gravity.

The coal is crushed, avoiding the production of dust as far as possible, until it will all pass through the half-inch sieve. The sample is then thoroughly mixed and a weighed amount of it (from 3 to 5 kg.) sifted over the quarter-inch and the twentieth-inch sieves. This divides it up into sizes $\frac{1}{2}$ to $\frac{1}{4}$, $\frac{1}{4}$ to $\frac{1}{20}$ and $\frac{1}{20}$ to dust. The quantity in each size is then weighed and expressed in percentages of the whole. The two larger sizes are now separated in the chloride of calcium solution as follows: A beaker holding about a liter is nearly filled with the solution, the coal put into it a little at a time and well stirred to thoroughly wet it and detach all air bubbles. The coal rises to the surface, while the slate and pyrite settle to the bottom. Enough of the coal should be put in at a time to make a layer about an inch thick when it rises to the top. This is now skimmed out with a little dish or a dipper and dropped into a large funnel, the neck of which is closed with a small perforated porcelain disc. More coal is now added to the solution and the operation continued until all of the given size is thus separated.

The coal in the funnel is then thoroughly cleaned from chloride of calcium by pouring water over it, allowed to drain, then spread out on paper, air dried and weighed. The chloride of calcium solution is then carefully poured off from the heavy material in the beaker, which is then washed out, dried and weighed. The material finer than $\frac{1}{20}$ in. is washed in the miner's pan. The coal is stirred up in water in the pan, and then by rocking the pan carefully the lighter portion is floated off and can be caught in a large dish where it is allowed to settle. The water is decanted off and the material air dried and weighed. The slate and pyrite left in the pan are also collected, dried and weighed. Each of the above products should then be analyzed for ash and sulfur. As a check, the analysis of the original coal should be computed from the analyses of these products and should agree very closely with that of the original sample. The lighter products from the pan may be stirred up in water, and the portions settling in about one minute separately weighed. The fine stuff floating off is determined by difference, and will constitute approximately the coal lost in washing.

A little practice is necessary in order to properly manipulate the pan; but the treatment of the fine stuff in the $CaCl_2$ solution is very unsatisfactory, and as it forms only a small portion of the whole, inaccuracies in the panning will have little effect. From a comparison of the results shown on the various sizes, it may be desirable to repeat the experiment, crushing the whole of the coal to $\frac{1}{4}$ in. or even to $\frac{1}{8}$ in. in order to separate very finely disseminated pyrite and secure a coal low in sulfur. But as the loss in washing falls almost wholly on the finer coal, the increase of the proportion passing the smallest sieve must be carefully noted.

If the coal is crushed to smaller sizes and then separated in the solution, all the finest dust must be first sifted out on a 60- or 80-mesh sieve, or it will clog up the filters and prevent the draining off of the solution. The dust can then be panned as usual.

References:

See Drown, *Trans.* Am. Inst. Mining Engrs., XIII, p. 341.
Stoek, *J. Soc. Chem. Ind.*, 1897, p. 304.

The Determination of the Heating Power of Coal

By the heating power of a fuel is meant the total amount of heat produced by the complete combustion of the unit weight of the fuel.

In order to simplify calculations in technical work it is convenient to define the unit of heat as the heat required to raise the unit weight of water the unit of temperature. If the unit of weight is the gram and the unit of temperature the degree Centigrade, the unit of heat is the calorie. If the units are the pound and the degree Fahrenheit, the heat unit is the British thermal unit.

With the heat unit defined as above, the number expressing the heating value of a fuel will be the same, whatever the unit of weight adopted, as long as the unit of temperature is unchanged. If the unit of temperature is changed, as, for instance, from Centigrade to Fahrenheit, the figure for the heating value will simply have to be changed in the inverse ratio of the dimensions of the units.

In the example quoted, as the ratio of the degree C. to the degree F. is $\frac{100}{180}$, heating powers in calories can be converted into heating powers in B.t.u. by multiplying them by $\frac{180}{100}$, or $\frac{9}{5}$.

The heating power of coke, anthracite and bituminous coal can be calculated with sufficient accuracy for many purposes from the ultimate analysis by Dulong's formula, as follows:

Heating power $= 8080°\text{C.} + 34{,}460(\text{H} - \frac{1}{8}\text{O}) + 2250\ \text{S}$.

On the fuels specified the results by this formula rarely differ more than 2 per cent. from those obtained with the calorimeter.

Where accurate determination of the heating value is required, the direct combustion in the bomb calorimeter should be made.

For a description of the several forms of this instrument, the methods of using them, and the precautions necessary in order to secure accurate results, see "Fuel" by Herman Poole; Mahler, Bulletin de la Societe de L'Encouragement de L'Industrie; Berthelot, Mechanic Chemique, and Longuimine, Bestimmung der Verbrennungs Wärme.

For a complete description and discussion of the determination of the calorific value of coals see "Coal," by Professor E. E. Sommermeier, McGraw-Hill Book Co., publishers.

CHAPTER XXXI

THE ANALYSIS OF GASES

The analysis of the following kinds of gases will be described: flue or chimney gases, blast-furnace gases and producer gas, coke oven and natural gases, mine air. Of course the composition of any kind of gas may vary greatly but the following analyses are typical:

Chimney gas	Blast-furnace gas	Producer gas	Natural gas	Coke oven gas
CO_2 8.6%	CO_2 13.5%	CO_2 6.3%	CO_2 0.2%	CO_2 2.0%
O_2 10.3	O_2 0.0	C_2H_4 0.6	CH_4 85.3	C_2H_4 1.9
CO 0.2	CO 25.5	O_2 0.0	C_2H_6 12.5	O_2 0.3
N_2 80.9	H_2 3.0	CO 23.7	N_2 2.0	CO 6.4
	CH_4 0.2	H_2 11.1		H_2 56.3
	N_2 57.8	CH_4 2.6		CH_4 19.0
		N_2 55.7		C_2H_6 2.0
				N_2 12.1

Mine air is simply air containing more or less CO_2, CH_4 and possibly CO. The gases are grouped as above because the analysis of the gases in the different groups calls for special procedure. The methods given are methods in wide technical use.

It must not be forgotten that the results obtained by measuring the reduction in volume of a gas sample when its constituents are absorbed are the results on the dry basis although the gas in the apparatus is saturated with water vapor. The reason is that when a given constituent is absorbed the water vapor corresponding to the amount of the constituent absorbed at the same time condenses, since with constant temperature the aqueous tension in the remaining gas remains constant.

Further, if the gas contains tar or heavy hydrocarbon vapors in the hot main, these will condense more or less completely when the sample is taken and will not be obtained in the analysis. They must be determined by special methods.

Any change in the temperature of the gas during analysis will produce error in two ways, first, according to the law that the volume of a gas is proportional to its absolute temperature; second, because of the

fact that any change in temperature will change the aqueous tension in a gas standing over water. Thus if 100 c.c. of gas at 20°C. and 745 mm. pressure suffers a drop of 2° in temperature the final volume will be $\frac{291}{293} \times 100 \times \frac{743}{745} = 99.05$ c.c. So that under these conditions a gas having no CO_2 would if analyzed for CO_2 show 0.95 per cent. CO_2 unless the correction were made. The factor $\frac{291}{293}$ is simply the ratio of the absolute temperature and the factor $\frac{743}{745}$ is the ratio of the atmospheric pressure minus the drop in aqueous tension to the atmospheric pressure. The general formula is,

$$V' = V \times \frac{T'}{T} \times \frac{P \pm a}{P}.$$ V is the original volume, V′ is

the volume sought, T is the original absolute temperature, T′ is the new absolute temperature, P is the barometric pressure and a is the change in aqueous tension.

The Analysis of Flue Gas

Flue gas contains CO_2, O_2, CO, N_2, and sometimes small percentages of SO_2 and hydrocarbons, and traces of oxides of nitrogen. The gas is usually saturated with water vapor, but this is not considered in the analysis, which refers only to the dry gas. The percentage of water in the saturated gas can be calculated from the temperature; if the gas is not saturated, its "dew point" (the temperature at which moisture begins to condense from the gas) must be taken, and the tension of the water vapor it contains found from this. If the temperature of the gas is above the boiling-point of water, draw a measured volume of it through a condenser, taking the temperature of the saturated gas as it comes out

Weigh the water collected from the condenser and add to it the moisture remaining in the gas, as calculated from its temperature after the cooling. Or draw the gas through a weighed calcium chloride tube and determine the increase in weight, after filtering out the dust by passing the gas through a tube packed with asbestos kept at 100°C.

Only the CO_2, CO and O_2 are usually determined in flue gas, the remainder being considered as N_2. But any thorough investigation of a flue gas would require the determination of hydrogen and methane.

In making the analysis, a measured volume of the gas is treated successively with a series of reagents that absorb the several constituents, the remaining volume being measured after each absorption. The gas

is measured in a graduated tube, which must be surrounded with a water jacket to keep the temperature constant during the time taken for the analysis.

The gas is always measured at the atmospheric pressure. As the time taken for the analysis is very short, it is assumed that the temperature and the barometer remain constant during the period. However, a thermometer should be suspended in the water jacket and several observations made.

Sampling the Gas.—The gas should be drawn from the flue by a pipe that crosses it at right angles and extends to within 6 in. of the further wall. The end of the tube should be closed with a cap, and the gas should be drawn into it through a number of holes about $\frac{1}{16}$ in. in diameter, drilled along the side of the tube at regular intervals not greater than 6 in. The nearest holes should not be less than 6 in. from the side of the flue. The diameter of the tube should be at least twelve times the diameter of the holes in the side. This will insure a uniform sampling across the flue.

Professor Lord carefully tested this point by inserting such a tube in air and gas for different portions of its length and analyzing the gas drawn from the tube. The composition of the issuing mixture was always proportional to the number of holes in the gas and in the air, air and gas being under atmospheric pressure.

The sampling tube can be made of iron, if the temperature of the flue does not exceed 340°C., as at that temperature iron, even if rusted or covered with soot, is without action on flue gas, neither the CO nor the CO_2 being affected. This point was tested by the writer by passing flue gas containing CO through a glass tube filled with iron tacks, also with rusted tacks and with soot and tacks. The tube was immersed in a bath of melted lead and the temperature of the lead measured by a nitrogen-filled high temperature thermometer. If soot and rust are present on the iron, action begins about 340°C., and is rapid at 400°C., CO being oxidized by the Fe_2O_3 and oxygen consumed by the soot, forming CO_2. With clean iron, however, there is practically no action at 400°C. As 340°C. is above the temperature at which most flue or blast-furnace gas is drawn off, the use of iron tubes is generally permissible. For flue temperature higher than 340°C., water-cooled tubes must be used for withdrawing the samples. For rapidly withdrawing a single sample from the interior of a furnace, an iron tube, open at the end and wrapped with $\frac{1}{4}$ in. of sheet asbestos tied on with wire, can be used. The asbestos cover is well soaked with water and the tube run into the furnace and the sample drawn. A tube so protected can remain in a white hot furnace for two or three minutes without the asbestos drying or the tube heating beyond a safe point. A silica tube is convenient for sampling

gases from a very hot place such as at the ports of an open-hearth furnace. Where there is a strong draft, as in a chimney flue, it is important that the opening by which the tube passes through the wall be well plastered up with clay, or air may be drawn in and reach the nearer holes and affect the sample. From the end of the sampling tube the gas is drawn continuously by a water or steam aspirator. If the gas sample is to be kept any time before analysis, it must be borne in mind that gases containing CO_2 cannot be preserved over water, as the CO_2 is rapidly absorbed. If confined over water the water should be covered with paraffin shavings. The writer has found that if the water be well covered with paraffin shavings a sample of gas with 10 per cent. CO_2 will not lose 0.10 per cent. CO_2 in three hours.

In most cases it is possible and far preferable to make the analysis at the furnace, especially where a series of analyses is required. Where this is not possible, as, for instance, on a locomotive engine test, the apparatus shown in Fig. 17 will be found very effective and convenient for drawing a series of samples at short intervals.

The sample tube, F, f, has a capacity of about 250 c.c.; the ends are closed with rubber tubes stopped with short glass rods J. A number of these sample tubes are provided; they are kept in a rack in a box, and are filled with water before starting out. In the apparatus itself A is a bottle of about a liter capacity, containing absorbent cotton to filter the gas. C is a small bottle containing a little mercury; it serves as a trap to prevent reversal of the gas current. The gas enters through E, and is drawn out through D by an aspirator at the rate of about 150 c.c. a minute.

Thus the bottle, A, will always contain a gas representing the average of several minutes. H is a "pressure bottle," connected as shown.

In taking the sample the apparatus is set up as shown; the gas is supposed to be flowing freely through the bottles A and D. A pinch-cock (not shown) on the rubber connection between the Y tube and the sample tube is opened and gas drawn in by lowering the pressure bottle, H, until the gas fills the tube and also the lower tube, G. The cock is then closed and the pressure bottle lifted, so as to put the confined gas under a little pressure; but the lower tube, G, must contain gas enough to prevent any water getting into the sample tube. The rubber connection with F is now pinched tight and the tube disconnected. It is then closed by inserting the glass rod into the rubber. The lower end is closed in the same way. The rubber tubes and stoppers on the sampling tube can be wired if necessary to keep them tight. As the gas is under a little pressure, any leakage during the disconnection will be out from and not into the gas.

The tube is now replaced by a second one and the apparatus is ready for drawing a new sample.

Fig. 18 shows a convenient arrangement for drawing a single sample rapidly, as, for example, through an asbestos-covered pipe such as was described.

The bottle C contains a little mercury and serves as a trap. The bottles A and B contain brine covered with paraffin shavings P. The gas delivery tube is connected with the tube F. B is filled with water by raising A, the air escaping through the mercury in C. Now A is lowered

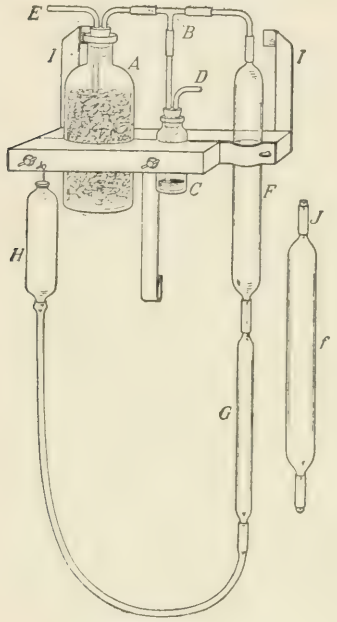

Fig. 17.

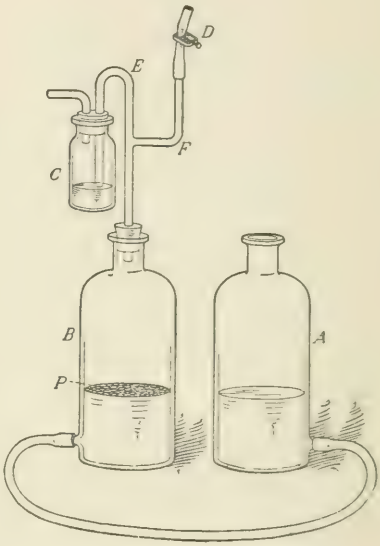

Fig. 18.

and the gas drawn in through F, the mercury preventing any return through E. In this way the gas can be drawn and emptied till all air is expelled, and then the bottle B filled and the pinch-cock D closed and the sampler removed. The bottles may be of large capacity so that the sample may be taken over many minutes. The water in B should be shaken with some of the gas in order to become saturated with it.

If it is desired to draw a sample continuously for several hours, the apparatus shown in Fig. 19 can be used. It will draw a sample at a nearly fixed rate per minute for several hours. It should be filled with

similar gas for some days and then emptied before use, as a new metal gas holder affects the sample a little at first.

The gas is drawn into the tank, A, through the cock, G, by the escape of the water at the bottom through the tube, B. The rate of this escape is kept uniform by the floating siphon, E, in the connecting cylinder, C. The tube, B, is large, so that the level of the water in the tank and the cylinder is the same, and the rate of flow from the latter is regulated by the constant head of the floating siphon carried by the float, D.

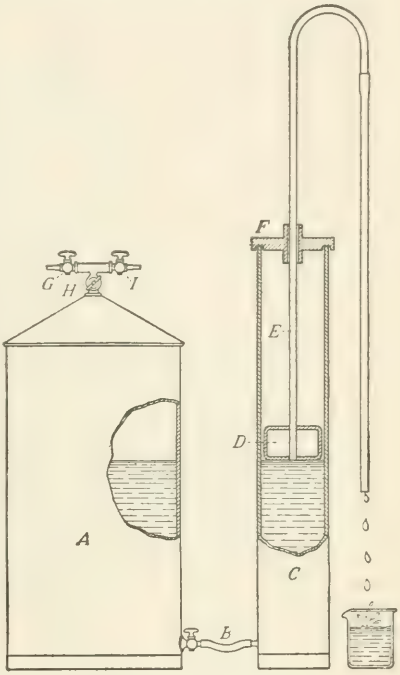

FIG. 19.

In analyzing the flue gas on boiler tests, one sample should be taken every 30 minutes. This will give a fairly accurate average for the period of 10 hours usually covered by the test. Experiments made by Mr. F. Hass in the Department of Metallurgy, Ohio State University, showed practically no difference in the results obtained by averaging samples taken every 30 minutes and every 15 minutes for 10 hours. Samples taken in the continuous sampler above described always show less CO_2, but otherwise agree closely with the average of the half-hour samples covering the same 10 hours, provided they are analyzed promptly. If the sample in the tank is allowed to stand for some time, the loss of CO_2 with a corresponding increase of nitrogen and oxygen may be very marked. The following two analyses illustrate the comparison for a 10-hour test. It shows the loss of CO_2.

	Average of 30-minute samples	Gas from tank
CO_2	11.1	10.4
O_2	8.0	8.25
CO	0.43	0.30
N_2	80.47	81.05

Apparatus.—The Orsat's apparatus is rapid and convenient for the analysis of flue gas, although the writer prefers the Hempel outfit, except when the apparatus must be carried around. Orsat's apparatus is shown as connected for use in Fig. 20. The gas from the flue is drawn into the bottle B through the tube A. B contains absorbent cotton to filter out soot from the gas. From B the gas passes down into the bottle D, where it bubbles through about an inch of water and then goes through F to the

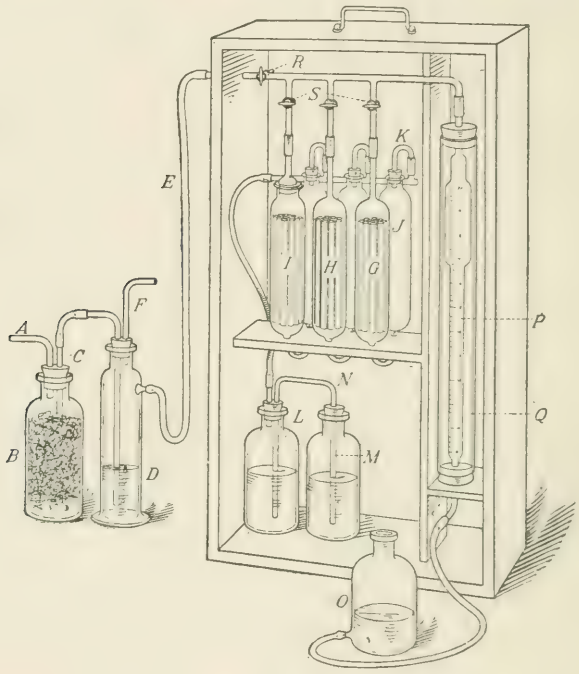

Fig. 20.

aspirator. If the rate of aspiration is about 150 c.c. a minute, and the bottle B of 500 c.c. capacity, D will contain a sample of the gas representing the average of some minutes. D is connected with the analyzing apparatus as shown. In the apparatus P is the gas measuring tube. Q is the water jacket. S shows the glass stop-cock that connects the gas tube with the reagent tubes, I, H, and G. These contain short lengths of glass tube to spread out the liquid and increase the active surface.

L and M are bottles arranged as a water seal to keep the air from the reagents in the tubes; they are connected with the rear bulbs of the tubes as shown. R is a three-way cock that serves to empty the gas from the apparatus. O is the pressure bottle for manipulating the gas in the measuring tube.

The apparatus should be protected from drafts of cold air, but, as the analysis is completed in 15 minutes, the water jacket on the measuring tube will prevent any appreciable change in temperature if ordinary care is used. All the stop-cocks should be well greased with vaseline. Two or three drops of H_2SO_4 should be added to the water in the pressure bottle, as this prevents it from becoming slightly alkaline and absorbing CO_2.

The water in the pressure bottle must be saturated with the gas to be analyzed, to prevent its acting on the sample. This is best done by running several analyses before the regular work begins. This will bring the water to a condition of saturation with the average gas and render it practically non-absorbing to the gas analyzed. Once in this condition the water can be used indefinitely. If new water is put in, the saturation must be repeated. The water in the pressure bottle must be at the same temperature as that in the burette jacket.

Preparation of the Reagents.—KOH solution. Dissolve 100 grams of the best quality potassium hydroxide in 300 grams of water. Let the solution stand in a closed bottle till any oxide of iron settles, and use only the clear solution. It is best to prepare a quantity of this and keep it some time before use. Carbon dioxide is easily and rapidly absorbed in the KOH forming K_2CO_3.

Potassium Pyrogallate.—This is the best absorbent for oxygen. Phosphorus is also frequently used but it is too easily "poisoned" so that it will not work. The writer always prefers the pyrogallate. It is made by dissolving 15 grams of pyrogallic acid, $C_6H_3(OH)_3$, in 100 c.c. of a solution of KOH, sp. gr. 1.55. The solution will absorb about 20 c.c. of oxygen per cubic centimeter.[1] It acts rapidly at first but as it becomes saturated with oxygen it acts more slowly. The relation of the pyrogallic acid to the alkali is important, for, if the concentration of alkali is too low, some CO may be given off when oxygen is absorbed.

[1] ANDERSON, *J. Ind. Eng. Chem.*, VII, 587.

The solution as above made will not evolve CO. At temperatures above 15°C. the absorption is rapid, the oxygen in 100 c.c. of air being absorbed in three minutes, but at lower temperatures the absorption is much slower. Of course CO_2 will be absorbed in this solution and it must be previously removed with KOH. If the gas contains only a little oxygen the pyrogallate solution is best made by dissolving 15 grams of pyrogallic acid in 150 c.c. of 30 per cent. KOH.

Ammoniacal Cuprous Chloride.—Dissolve 450 grams of ammonium chloride and 400 grams of cuprous chloride in 1500 c.c. of water. For use the solution is diluted with one-third its volume of ammonia water, sp. gr. 0.9. Some metallic copper should be kept in the solution to keep it active. One cubic centimeter will absorb about 16 c.c. of CO. The reaction is $2CuCl+2CO=Cu_2Cl_22CO$. However, this compound is very unstable and after a certain amount of it has been formed in the solution it begins to decompose and to give up CO. Consequently in all work where much accuracy is required it is absolutely necessary that the greater part of the CO be first absorbed in one cuprous chloride pipette and then the remaining CO be absorbed in a pipette containing freshly prepared cuprous chloride solution. The second one, after it has been used a number of times, is made the first and a fresh supply is put in the second.

The cuprous chloride also absorbs oxygen, hence the oxygen in the sample must be removed before the CO is absorbed in the cuprous chloride. Cuprous chloride will also absorb acetylene, ethylene, etc.

To fill the apparatus: Remove the old solution by first driving air over the gas tube into the absorbing bulbs. This is done by raising the pressure bottle and forcing the liquid all into the rear bulbs. Then empty each by a small siphon first filled with water and inserted to the bottom of the bulb. Now fill the first rear bulb, J, with the KOH solution. This serves to absorb CO_2 and also SO_2 and H_2S. It acts rapidly and completely and one filling will serve for from fifty to sixty gas analyses before its action begins to be too slow.

Put a good-sized funnel into the second rear bulb and weigh into it 30 grams of pyrogallic acid. Wash this down into the bulb with 200 c.c. of KOH solution. If the apparatus will not

hold the volume of solution, take less and reduce the pyrogallic acid proportionately; if it requires more add more.

The third bulb is filled with the cuprous chloride solution. The glass tubes in this bulb contain spirals of copper wire, which keep the solution reduced.

Process of Analysis.—Fill all the reagent bulbs to the mark on the capillary tubes by opening the proper stop-cocks and lowering the pressure bottle carefully till the liquid rises to the right point. Do this with one bulb at a time, and on no account try to set the level of the liquid by opening or closing the stop-cocks. Bring it to the right point by raising or lowering the pressure bottle, and then close the stop-cock. Proceeding in this way, the fluid will never be drawn up into the stop-cock. Should such an accident happen, the stop-cock must be immediately taken out, washed, and then relubricated with vaseline. The alkaline liquid, if allowed to remain in the glass stop-cock, would soon cause it to stick hopelessly. Now set the three-way cock so that the opening to the side is connected with the measuring tube. Raise the pressure bottle till the liquid fills the tube to the mark on the capillary. Turn the cock so as to close this connection and open the one to the sample inlet tube, lower the bottle and draw in slowly 50 or 60 c.c. of gas. This should be enough to completely wash out air in the connecting tubes. Again reverse the stop-cock, lift the bottle and run this gas, which is contaminated with that left in the connections and capillaries, out through the side tube. Now again reverse the stop-cock and draw in the sample of gas for analysis, lowering the bottle until the gas fills the measuring tube to some distance below the zero mark. Close the cock and set the pressure bottle on a support a little above the level of the zero point. Pinch the rubber near the bottom of the burette, open the cock to the side and carefully let the liquid run in by releasing the pressure of the fingers until it reads exactly zero on the tube. Now close the cock carefully, take down the bottle, and read the volume of the gas after equalizing the pressure by bringing the surface of the liquid in the bottle to the level of that in the tube. The reading should be exactly zero. If it is 0.1 or 0.2 c.c. off, this can be corrected by raising or lowering the level of the water in the pressure bottle until the reading is zero, and making all

subsequent readings in the analysis after giving the leveling bottle the same relative elevation.

The measuring tube now contains 100 c.c. of gas. Open the stop-cock into the potash bulbs and run the gas over by raising the pressure bottle. Be careful to so hold the bottle that the liquid will rise only to the mark in the gas tube. Now draw the gas back in the same way, run it over again and again back. Bring the potash solution carefully to the mark in its tube, close the stop-cock, wait at least 30 seconds for the liquid to drain down the side, level as before and read the volume. Transfer a second time to the potash, draw it back and read the volume again. If it does not agree with the first reading, run it over a third time. With fresh potash solution, the second reading should always check the first. The decrease in volume is the CO_2. Now proceed in the same way with the other tubes, using the pyrogallic solution first and then the cuprous chloride. With the pyrogallate tube, the gas should be run over two or three times rapidly before taking a reading, so that the dark saturated solution forming on the walls of the bulb may not remain long in contact with the gas, as this might lead to the formation of CO. The liquid draining down the side of the bulb will show by its change of color when it is absorbing oxygen. As soon as the oxygen is all absorbed, the liquid on the sides of the bulb will not turn brown as the gas reaches it. Always get two readings that agree before proceeding to the next tube. The corresponding decreases in volume give the oxygen and the CO. The residual gas is estimated as N_2. It will contain any H_2 and CH_4 present in the original gas, but these are rarely present in chimney gases in measurable amounts. When the analysis is finished, run out the residual nitrogen, leaving the measuring tube full of water. Now everything is ready for the next test.

Extreme care should be taken to avoid getting any of the absorption solutions into the connection or measuring tubes. Should this happen, they must be washed out and the water in the pressure bottle changed before starting a new analysis, as gas might be absorbed in filling the apparatus. The Orsat's apparatus may be used for the determination of CO_2 and CO in the gas from the iron blast furnace. In this case the residual gas invariably contains hydrogen and methane and should be kept for further analysis.

If the pipettes are of the "bubbling" type, the absorption is more rapid.

Blast Furnace and Producer Gas

These two gases are analyzed in the same way. The writer prefers the Hempel apparatus for the analysis of these gases rather than special built up apparatus, because the Hempel is more convenient and is accurate. It is the writer's experience that results with the Hempel apparatus can with care be made accurate to 0.05 per cent. When greater accuracy than this is desired it is necessary to use some form of apparatus such as the one evolved by Mr. Burrell of the Bureau of Mines and shown on page 291, or such as the Haldane apparatus. The complete analysis of a producer gas can be made in less than a half hour. What was said concerning sampling and storage of gas at the beginning of this chapter applies here. If the sample is taken over water, as when a long time sample is taken, the surface of the water must be covered with paraffin shavings.

Apparatus Used.—A is a single pipette containing 30 per cent. solution of KOH used for absorbing CO_2. B is a pipette filled with fuming sulfuric acid. The small upper bulb is filled with glass beads in order to give a larger surface of contact between the gas and the acid. This is used for absorbing the "illuminants" or unsaturated hydrocarbons such as ethylene, C_2H_4, propylene, C_3H_6, etc. C is a double pipette containing alkaline pyrogallate for oxygen. D D, double pipettes containing ammoniacal cuprous chloride, are precisely the same as C. It is not necessary to use both on gases containing but traces of CO but if the gases are blast-furnace gas, or producer gas, or coke-oven gas, or water gas it is necessary to use two cuprous chloride pipettes and even three are sometimes used. E is a combustion pipette containing a platinum spiral which can be heated with an electric current. It is made from a single pipette for solid reagents. One bulb has been cut off and used for the leveling bulb. A capillary tube with a stop-cock is attached. The pipette is filled with mercury and connected to a leveling bulb with heavy rubber tubing. The combustion pipette sets in a basin to catch the mercury should the tube break. F is the burette connected with a leveling bottle G. The burette must be water jacketed and a thermometer should hang in the water of the jacket. It is convenient to have the stop-cock a three-way one

but not necessary. H is a capillary tube with an internal diameter between 0.5 and 1.0 mm. or about $\frac{1}{40}$ in.

The rubber tubes on the pipettes should be made of thick-walled pure gum and should be wired to the pipettes by passing the wire around twice or more to prevent leakage. The rubber

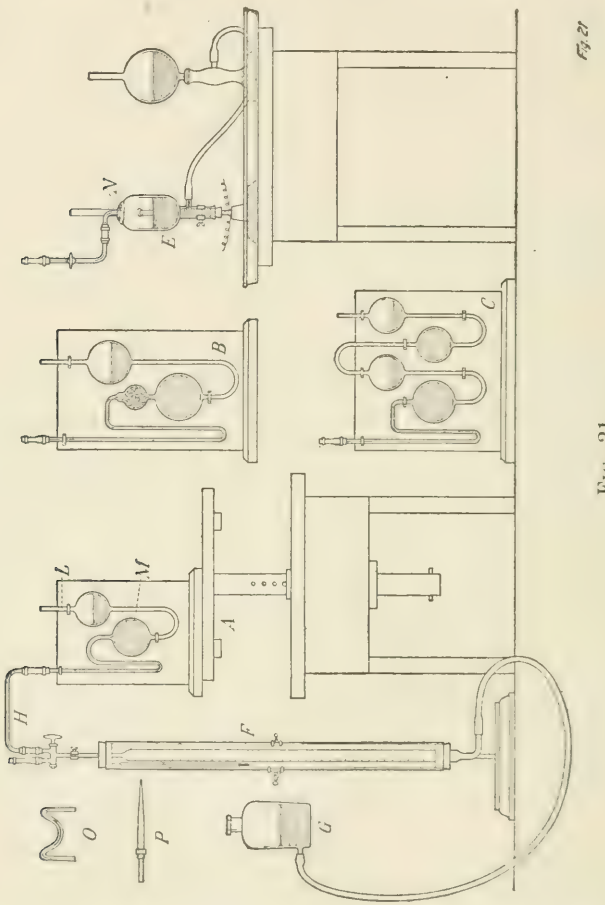

Fig. 21.

tube should project beyond the end of the capillary of the pipette about $1\frac{1}{8}$ in. but not so long but that the air in the tube can be driven out by squeezing it between the thumb and forefinger. Also, and this is important, the tube should have a band of elastic rubber about it as shown in the cuts, in order to make a tight

connection when the capillary on the burette is pushed in the tube. This band is put on as follows: Cut a piece of pure gum tubing a little smaller in diameter than the rubber tube on the pipette and about a quarter of an inch long. Push this on a tapering glass tube (P, Fig. 21) until it is at the big end, which should be as large in internal diameter as the rubber tube on the pipette. Push the rubber tube into the glass tube about ¼ in. and then push the rubber band off the glass tube onto the rubber tube. This will make the burette capillary fit in the rubber tube without leaking gas and without the bother of tying the connection each time.

Filling the Pipettes.—To fill the single pipettes, simply pour the reagent in the large tube L until there is enough to fill the bulb M and to have about ½ in. of the reagent in the other bulb.

To fill the double pipettes, first pass an oxygen and carbon monoxide free gas, such as natural gas or hydrogen, through the pipettes until the air is displaced. Then attach to the capillary of the pipette a rubber tube the end of which dips into the reagent which is to be put in the pipette, then suck on the other end of the pipette until enough of the reagent has entered to fill the first bulb full and about ½ in. in the second. A little experience makes this easy. Then pour into the rear bulb 125 c.c. of water to act as a water seal to keep out the air. The purpose of filling the bulbs with a neutral gas is to prevent the weakening of the reagent by air in the bulbs.

The reagents are prepared as directed on page 271 et seq.

Process of Analysis.—First see that the water in the burette jacket is at the same temperature as that in the leveling bottle. The water in the leveling bottle should be shaken with some gas similar to that to be analyzed and so should the absorption solutions in the pipettes in order to saturate the liquids with the gas other than the constituent to be absorbed in the solution. This is most readily done by making a preliminary analysis of the gas. Then see that the burette is tight by taking a reading, then raising or lowering the pressure bottle and allowing the gas to stand under a pressure or vacuum for several minutes. Then take another reading. The readings ought to agree exactly. In reading the burette hold a finger or piece of paper back of the burette and a little below the meniscus so as to illuminate the

bottom of the meniscus and make the reading sharp. With care one can be sure of the reading to within less than 0.05 c.c. The water in the pressure bottle should contain about 0.5 per cent. H_2SO_4.

Now raise the pressure bottle until all gas is out of the burette and water drops from the end of the capillary. Also wash the capillary by dipping the end of it in acidulated water to remove all alkali. Then attach the rubber tube of the vessel containing the sample to the burette capillary, first taking care to drive all air out of the rubber tube. Then lower the pressure bottle of the burette and raise the pressure bottle of the vessel containing the sample and open the stop-cock on the burette and draw in the gas until a little more than 100 c.c. has been drawn in. Close the stop-cock and detach the sample vessel. Allow the burette to drain about 30 seconds. Raise the pressure bottle until the bottom of the meniscus is just on the zero (or 100 c.c.) mark, pinch the rubber tube connecting the burette and bottle and open the stop-cock momentarily to put the gas under atmospheric pressure. Close the cock and level the water in the burette exactly with the water in the bottle and take the reading. It should read exactly zero (or 100 c.c.). At the same time read the temperature of the jacket water.

Now attach the KOH pipette to the capillary of the burette as follows: squeeze the rubber tube on the pipette between the thumb and forefinger so that all air will be driven out of the tube and the KOH will fill the capillary of the pipette. Then push the capillary of the burette into the rubber tube in such a way as not to drive air into the tube and until the ends of the capillaries are in contact. The KOH should extend nearly to the top of the pipette capillary. Make a mental note of its position. Now open the stop-cock and raise the pressure bottle and drive all the gas over into the pipette. Close the cock and shake the KOH pipette vigorously for 20 or 30 seconds, then raise the pressure bottle and run a few drops of water into the pipette to wash all KOH which was splashed into it out of the capillary. Then lower the pressure bottle and draw the gas back into the burette until the KOH rises in the capillary of the pipette exactly to the same height as it was at the beginning. Allow the burette to drain as long as before and take the reading of the burette care-

fully, also read the temperature of the jacket. The decrease in volume (if there has been no temperature change) is the percentage of CO_2 in the gas. To make sure that the CO_2 is all absorbed repeat the above operation. The reading should be the same as before. If not, run a blank determination by again repeating the operation of driving the gas into the KOH pipette, etc., and again read the burette after the usual draining. If there is a further change of volume, either positive or negative, it shows that there is a leak or that the temperature is changing. Twice this change in volume should be added to or subtracted from the second reading. By taking this trouble of running a blank the results can be relied upon to 0.05 per cent. For most technical work such care is not necessary but should be taken occasionally to check up the work.

Now remove the KOH pipette and attach the fuming sulfuric acid pipette in the same way, making mental note of the position of the acid in the capillary. The connection must be especially tight as it requires considerable pressure to drive the gas into this pipette. Raise the pressure bottle and drive the gas into the burette *but do not let any water get into the sulfuric acid pipette.* Pass the gas back and forth between the burette and pipette three times, then bring the sulfuric acid back to the original place on the capillary. The gas now has sulfuric acid vapors in it which must be removed by passing the gas into the KOH pipette and shaking vigorously. Finally bring the gas back into the burette and read the change in volume and temperature. If there has been no temperature change, the decrease in volume is the percentage of "illuminants," chiefly C_2H_4. The C_2H_4 is changed into ethionic acid, $C_2H_6S_2O_7$. Any acetylene is changed to $C_2H_4SO_4$ and benzene to $C_6H_6SO_3$. Since blast-furnace gas contains no heavy hydrocarbons the fuming sulfuric acid is not used when blast-furnace gas is analyzed.

It is well to run a blank on this determination occasionally.

Next attach the pyrogallate pipette and manipulate just as with the KOH pipette except that the shaking of the gas in contact with the solution should be much longer. The decrease in volume is the percentage of oxygen. To make certain of complete absorption of the oxygen it is necessary to run the gas into the pipette again. There should be no change in volume.

Next attach the ammoniacal cuprous chloride pipette and manipulate as with the pyrogallate pipette. The CO is absorbed slowly and the pipette should be shaken at least 100 times, and if the cuprous chloride has been used before, the gas must be run into a second cuprous chloride pipette and shaken 100 times. This is always the best way if the gas contains more than 2 per cent. of CO. When the first pipette gets too slow in its action, it is emptied and filled with fresh solution and used as the second pipette while the other one is used first.

The gas now has left in it only hydrogen, methane, and nitrogen.

The hydrogen and methane are determined by combustion in the combustion pipette. They may be determined by explosion in an explosion pipette but the writer does not like the explosion method. The combustion method is carried out as follows: Attach the combustion pipette to the capillary of a burette containing oxygen and run in enough oxygen to uncover the platinum wire and its connections, but do not use more than 40 c.c. Measure the oxygen carefully and the temperature of the burette from which it was taken. Close the stop-cock of the pipette and attach it to the capillary of the burette containing the gas. Connect the wires from a source of electricity to the terminals of the wires of the combustion pipette. Turn on the current until the platinum wire in the pipette is at a dull yellow of nearly the same brightness as an ordinary incandescent light carbon filament. Record the temperature of the gas, then open the stop-cocks on the burette and the pipette and run the gas into the pipette slowly, in order, in the case of producer gas, to prevent an explosion or melting of the platinum. The mercury in the leveling bulb of the pipette should be at about the same level as the mercury in the pipette in order to avoid leaks due to the great pressure caused by considerable difference in levels of the mercury. After the gas is all in the pipette, close the pipette stop-cock and continue the combustion for several minutes. The pipette should be kept cool during the combustion by water dripping on the cotton, N Fig. 21, around the top. Now shut off the electric current and run the residual gas back into the burette. Allow the gas to cool a minute and then read the volume and temperature. If there has been any change in temperature make the proper correction. Call the

contraction in volume C. Now attach the burette to the KOH pipette and determine the CO_2 produced by the burning of the CH_4. The methane in the gas was the same in volume as the CO_2 produced by its combustion, and since the original sample was 100 c.c. the volume of CO_2 produced in cubic centimeters is the percentage of methane in the gas sample. The contraction in volume due to the burning of the methane is twice the volume of the methane, and this contraction subtracted from the total contraction C on burning gives the contraction due to the burning of the hydrogen, which multiplied by $\frac{2}{3}$ gives the volume and percentage of the hydrogen.

The reactions are: CH_4 (1 vol.)$+2O_2$ (2 vol.)$=CO_2$(1 vol.)$+$ $2H_2O$. Since the H_2O condenses, the contraction is twice the CH_4.

$2H_2$(2 vol.)$+O_2=2H_2O$. Since the H_2O condenses, the hydrogen is equal to two-thirds of the contraction when it is burned.

The total time required for the analysis of the gas is about 25 minutes.

Notes on the Process.—The two cuprous chloride pipettes may be permanently connected by means of a T capillary, with a stop-cock in each branch going to a pipette, and the third branch connected to the burette. In this way only one operation of connecting the cuprous chloride pipettes to the burette is necessary, although each pipette works separately.

If the stop-cock on the burette is a "two-way" one it is convenient to attach the KOH pipette permanently to one of the ways because the KOH pipette is used three times during the analysis, and a permanent attachment of it saves the time of three operations. This idea has been carried out to the extent of having a stop-cock with enough different "ways" to have a permanent attachment for each pipette.

After each time that a pipette is connected to the burette a drop of water should be placed on the top of the rubber connection, so that if the connection is leaking the bubbling of gas through the drop may be seen.

The combustion pipette should hold about 150 c.c. The platinum wire should be inserted far enough in so that 40 c.c. of gas in the pipette will uncover the wire and prevent the mercury from short-circuiting the current. It is best to wrap the top of the pipette with cotton and keep water dripping on the cotton during the combustion so that

the glass will not get so hot that it is liable to crack. The pipette must be surrounded with a wire netting or gauze so that the eyes of the operator will be protected if an explosion should take place. It is convenient to have a stop-cock on the combustion pipette, but is not necessary. If a stop-cock is not used, it is necessary to close the rubber tube on the capillary with a glass plug when the pipette is moved from the oxygen burette to the burette containing the gas.

The electric connections for the platinum wire are easily made as follows: To the end of a copper wire about 6 in. long fasten a piece of platinum wire of 20 gage and 1 in. long and pass it through a piece of glass tubing 5 in. long and ¼ in. internal diameter. Inside this tube pass a smaller glass tube with another copper wire with platinum end. The platinum wires should project ½ in. beyond the end of the larger glass tube which should be 1 in. longer than the other. Now heat the large glass tube so that the glass will soften and the end will close about the platinum wires. It is well to squeeze the softened glass with a pair of pliers to close the ends perfectly and to leave no thick ball of solid glass which is apt to crack when heated. The other end of the outer tube should be constricted so that the inner tube will not fall out. Pass the tubes through a hole in a rubber stopper which fits the opening in the bottom of the combustion pipette. Connect the platinum ends with a 30-gage platinum wire, about 1½ in. long and coiled in several coils. The platinum coil should be about ¾ in. from the top of the pipette. It is best to provide a second platinum coil in the pipette, connecting it to one of the terminals above described and to an iron rod passing through the mercury and the stopper. Then if one coil melts, the other can be used.

The platinum wire must be heated to a dull yellow or the combustion is likely to be incomplete. The wire may be heated by about three or four dry cells or better by the current through six 16-candle-power electric lights placed in parallel on a 110-volt circuit. That is, a current of about 3 amperes is required, depending, of course, on the diameter of the wire. If the wire is heated hotter than a dull yellow a slight error is caused due to formation of N_2O_4.

When a gas contains ethane as well as methane and hydrogen, which is not the case with producer or blast-furnace gas, the hydrogen must be determined separately as directed under the analysis of coke-oven gas. Of course the hydrogen in producer or blast-furnace gas may be determined separately, but this is not necessary. If the gas contains hydrogen and no methane the combustion pipette may be filled with water instead of mercury. Blast-furnace gas contains only about 0.2 per cent. methane. If the gas contains both hydrogen and methane and the hydrogen is removed first, the combustion of methane may be made without mercury.

Gas Analysis without use of Cuprous Chloride.—Instead of absorbing the CO in cuprous chloride and then determining the hydrogen and methane by combustion, the carbon monoxide, hydrogen and methane may be all determined together by combustion without having to use the cuprous chloride. This applies only to gases like producer and blast-furnace gases which have no hydrocarbons higher than methane.

Process of Analysis.—Carry out the combustion exactly as above directed. Measure the decrease in volume after combustion, and then determine the CO_2 produced by the combustion by passing the residue into the KOH pipette. Then determine the amount of oxygen left after the combustion by absorbing it in pyro solution. Also carefully determine the amount of oxygen in the volume of oxygen used by passing the same volume of oxygen through the pyrogallate pipette. The difference between the two gives the amount of oxygen used. Calculate the results as follows: The reactions of combustion are as given above for hydrogen and methane and as follows for carbon monoxide: $2CO$ (2 vol.) $+ O_2$(1 vol.) $= 2CO_2$(2 vol.). Let x = hydrogen, y = methane and z = carbon monoxide. Then we have the following equations:

Contraction during combustion $= \frac{3}{2}x + 2y + \frac{1}{2}z.$
Carbon dioxide produced $= y + z.$
Oxygen consumed $= \frac{1}{2}x + 2y + \frac{1}{2}z.$

Combining these equations we get the relations:

Hydrogen = contraction minus oxygen consumed.

Methane = oxygen consumed minus $\frac{1}{3}$ contraction minus $\frac{1}{3}$ CO_2 produced.

Carbon monoxide = $\frac{4}{3}$ CO_2 produced plus $\frac{1}{3}$ contraction minus oxygen consumed.

Notes on the Process.—This method requires less time for manipulation but more time for calculation than the one previously given. They are about equally accurate.

There is a correction necessary for accurate work when a gas is burned which gives a large amount of CO_2. It is due to the fact that the molecular volume of CO_2 is 22.26 liters while that of CH_4 is 22.44 liters and of CO is 22.39 liters. That is, the CO_2 produced by burning 100 c.c. of methane is 99.20 c.c. instead of 100 c.c., because CO_2 departs considerably from being a perfect gas. So that when CO or CH_4

are burned, the contraction in volume should be corrected by subtracting from it 0.8 per cent. of the volume of CO_2 produced and the volume of the CO_2 should be increased by 0.8 per cent. of the measured amount of CO_2 in order to calculate the volume of the methane or the CO.

The determination of dust in unwashed blast-furnace gas is an exceedingly difficult proposition. For the apparatus and details used for this determination see Touzalin and Brady, Jour. Ind. Eng. Chem., III, pp. 662–670.

The Copper Oxide Method

The methods described above are, in the author's opinion, very reliable and accurate. However, H. H. Worrell recommends Jäger's method modified. (See Met. Chem. Eng., XI, 245.) In outline it is as follows: Analyze the gas just as above described until the oxygen is removed. Then connect between the burette and a single Hempel pipette filled with acidified water, or, better, with mercury, a silica tube, ¼ in. bore by 7 in. long. This tube is filled with copper oxide and surrounded with an air bath (Eimer and Amend catalogue No. 2073). The air bath is then brought to 250°C. and the gas in the burette is slowly passed through the tube and back again until the hydrogen is all burned which will require 6 to 8 passes. Cool the tube, return the gas to the burette so that the water in the pipette is at the original level in the capillary and read the contraction in volume. The contraction is the volume of the hydrogen present in the gas plus the oxygen that was in the tube. Then pass the gas into a KOH pipette and determine the CO_2 formed by the oxidation of the CO. The volume of CO_2 found is the same as the volume of CO that is present in the gas.

Now heat the silica tube to redness and pass the gas back and forth until the hydrocarbons are all oxidized. Cool and measure the volume. If an increase in volume is observed it is due to ethane and is equal to the ethane present. Then pass the gas into the KOH pipette and measure the CO_2 absorbed. The CO_2 found minus twice the volume of the ethane is equal to the methane.

The amount of air held by the silica tube can be found once for all for the correction of the hydrogen determination, but it is better to fill the tube with nitrogen. The copper oxide must be reoxidized after a determination by drawing air through the hot tube.

The Analysis of Coke-oven Gas.—Up to the combustion the analysis of this gas is carried on in exactly the same manner as for producer gas, except for the following: Since coke-oven gas has a rather large amount of "heavy hydrocarbons" the absorp-

tion of them in the fuming sulfuric acid should be given more time. After determining the "heavy hydrocarbons" run the gas over into the sulfuric acid to see if a further contraction is obtained. If it is, more time for the absorption must be used.

About 90 to 100 c.c. of oxygen must be used for the combustion of the entire combustible residue. This is run into the combustion pipette and then the spiral is heated to a dull yellow and the gas run into the pipette very slowly in order to prevent an explosion. It is best to set the pressure bottle, attached to the burette, up high with a screw-cock on the rubber connection closed. Then open the screw-cock just enough so that the gas will all be driven into the combustion pipette in about five minutes. The top of the pipette should be kept cool as directed under the analysis of producer gas. After the gas is all in the pipette the spiral should be kept hot for a few minutes.

Coke-oven gas may have some ethane in it; coal gas is sure to have. In such a case it is necessary to make a separate determination of hydrogen by the palladiumized asbestos method, for hydrogen cannot be determined when a mixture of hydrogen, methane and ethane are burned together. The method is given below.

Determination of Hydrogen by Combustion in Contact with Palladium.—When a gas containing hydrogen in the presence of methane and ethane is mixed with oxygen and passed over palladium heated to 90° to 100° the hydrogen is completely burned to water but the methane and ethane are unaffected if the temperature is not allowed to rise too high. If the gas contains much hydrogen it should not be passed over the palladium so fast as to cause the palladiumized asbestos to glow, for then some methane will be oxidized.

The palladiumized asbestos is prepared as follows: Dissolve 1 gram palladium in aqua regia, evaporate the solution to dryness on a water-bath, so as to remove any adhering hydrogen chloride as completely as possible, and dissolve the palladium chloride thus produced in a very little water. To this add a few cubic centimeters of a cold saturated solution of sodium formate and sufficient sodium carbonate to produce a strongly alkaline reaction. Now introduce 1 gram of very soft, long-fibered asbestos, which, if any excess of water has been avoided, absorbs the whole liquid and forms with it a thick paste. This is dried at a gentle heat, by which process black, finely divided

palladium is uniformly precipitated upon the asbestos-fiber. In order to make the palladium adhere, the asbestos thus prepared must be heated on a water-bath till completely dry, then soaked in a little warm water, put into a glass funnel, and freed from all adhering salts by thorough washing, without removing any palladium. After drying, the substance exhibits a dark gray color, has a slight tendency to stain the fingers, and contains 50 per cent. palladium. It possesses a very high degree of chemical activity; in the perfectly dry state it can cause the combination of hydrogen and oxygen even at the ordinary temperature, but in order to secure this result it is always employed in the heated state.

For the preparation of the capillary combustion tubes, employ capillary glass-tubing of about 1 mm. bore and 6 mm. outside diameter, cut in pieces 16 or 18 cm. long and bent as shown at O, Fig. 21. The asbestos-fiber must be introduced into them before bending off the end, in the following way: a few loose fibers of the palladium-asbestos are laid alongside each other on smooth filter-paper up to a length of 4 cm.; they are moistened with a few drops of water, and by sliding the finger over them, are twisted into a fine straight thread, which in the moist state has the thickness of stout sewing-cotton. This thread is grasped at one end with the nippers, and, without bending or nicking, is slid from above into the capillary tube, which is held vertically. This is then filled with water by means of the washing-bottle, and by jerking or by drawing off the water the asbestos-thread is brought into the center of the tube. This is now allowed to dry in a warm place. It is well to have small bulbs blown near each end of the tube to prevent films of water getting to the palladium.

Procedure for the Determination of Hydrogen.—After the CO has been determined by absorption in cuprous chloride, transfer one-half of the remaining gas back into the cuprous chloride pipette, keeping the other half in the burette. This may contain as high as 30 c.c. of hydrogen. Draw into the burette 15 c.c. of oxygen and then enough air to fill the burette to 100 c.c. There will now be about twice as much oxygen present as is theoretically necessary to burn the hydrogen. Carefully read the burette and its temperature. Then attach the palladiumized

asbestos capillary, place a small beaker of water under it so that the capillary is immersed, heat the water to boiling and attach the other end of the capillary to a Hempel pipette containing only acid water. Pass the gas through the palladium capillary at the rate of about 15 c.c. per minute, taking care that the gas does not pass through so rapidly that the heat generated by the burning hydrogen causes the palladium to glow. Do not allow the water of the burette or pipette to rise up to the palladium. When the gas has all passed over, draw it back into the pipette and carefully read the volume and temperature. The hydrogen should be all burned, but to make sure, again pass the gas over and back. There should be no change in volume the second time. The total contraction multiplied by $\frac{2}{3}$ gives the hydrogen present and this multiplied by 2 gives the percentage of hydrogen.

Now to see if any methane has been burned (none should have been if the palladium was not allowed to glow) pass the gas into the KOH pipette. If any CO_2 is found some methane was burned and a correction must be made.

Determination of the Methane (and Ethane).—Measure about 75 c.c. of oxygen and pass it into the combustion pipette. Heat the platinum spiral to a bright yellow and carry out the combustion as directed under the analysis of producer gas except that the combustion must be made more carefully and slowly because of the more inflammable nature of the gas. After the combustion, determine the contraction in volume and the CO_2 produced.

From the contraction in volume obtained, subtract the contraction due to the burning of the hydrogen. This gives the contraction due to the burning of the methane and ethane. Then let X = the CH_4 and Y = the C_2H_6. We have the relations:

$$\text{Contraction} = 2X + 2.5Y$$

and

$$CO_2 = X + 2Y$$

Solving we get

$$X \text{ (or methane)} = \frac{4 \times \text{contraction} - 5CO_2}{3} \text{ or } CH_4 = CO_2 - 2C_2H_6$$

and

$$Y \text{ (or ethane)} = \frac{4CO_2 - 2 \times \text{contraction}}{3}$$

The reaction for the combustion of ethane is:

$$2C_2H_6\ (2\ \text{vol.}) + 7O_2\ (7\ \text{vol.}) = 4CO_2\ (4\ \text{vol.}) + 6H_2O\ (\text{condensed}).$$

The results obtained for methane and ethane when multiplied by two give the percentage in which they were present in the sample. The oxygen consumed may be determined to check the results.

Notes on the Analysis of Coke-oven Gas.—The gas is apt to contain some hydrocarbon vapors such as C_5H_{12}, etc. For their determination see page 290.

The fuming sulfuric acid absorbs the olefins, C_nH_{2n}, acetylene, C_2H_2, the benzene hydrocarbons, such as C_6H_6 and the higher paraffin hydrocarbons such as C_5H_{12} and C_6H_{14}. If it is desired to know how much benzene is present, the total heavy hydrocarbons are determined by absorption in fuming sulfuric acid. Then in another sample they are absorbed with a standard bromine solution. The bromine combines with the ethylene to form $C_2H_4Br_2$ but does not combine with the benzene. The excess bromine is titrated with potassium iodide and sodium thiosulfate, from which the ethylene can be calculated. (Haber and Oechelhauser, Berichte, XXIX, p. 2700.) At coke-oven works the benzene is determined by passing the gas through four absorbing bottles containing cooled paraffin oil, sp. gr. 0.89, boiling-point 360°C. The gas dried by passing over $CaCl_2$ is passed through these bottles cooled by ice, the bottles connected by glass, not by rubber, until a large volume has passed through at about 2 c.c. per second. The increase in weight of the bottles gives the weight of benzene absorbed.

Naphthalene is determined by passing several cubic feet of the purified gas through a N/20 picric acid solution, filtering off the naphthalene picrate and titrating the excess picric acid with N/5 $Ba(OH)_2$ using phenolpthalein indicator (see White, "Gas and Fuel Analysis.")

Benzene is absorbed by water and KOH solution, therefore if the gas contains benzene either the fuming sulfuric acid must be used before the KOH or the KOH must be saturated with benzene. Alkaline pyrogallate absorbs a small amount of the higher paraffine (Bul. 42, U. S. Bureau of Mines).

Upon prolonged contact fuming sulfuric acid will absorb some methane and ethane. This, however, is negligible if the time of contact is not prolonged beyond 5 or 10 minutes. The same is true of bromine.

According to Fritzche (*Z.* f. angew. Chem., 1896, p. 456) ethylene can be separated from butylene by sulfuric acid, sp. gr. 1.62, which dissolves butylene but not ethylene.

Cuprous chloride absorbs ethylene and acetylene. These gases therefore must be removed before the CO. It also slightly dissolves the higher paraffins.

Analysis of Natural Gas

According to the experience of Mr. Burrell of the Bureau of Mines, the natural gas of this country does not contain any unsaturated hydrocarbons, although a slight absorption is obtained with fuming sulfuric acid due to the absorption of other hydrocarbons. Neither does the gas contain carbon monoxide or hydrogen. These gases should never be reported as present in natural gas unless a qualitative test is obtained for them. The test for unsaturated hydrocarbons is made as follows: Prepare a 1 per cent. neutral solution of palladous chloride, $PdCl_2$, containing 5 per cent. sodium acetate and pass a large volume of the gas through the solution after first passing it through a KOH solution to remove any H_2S present. If there is any ethylene in the gas it will reduce the palladium and a black precipitate of palladium will settle out. Any CO will also reduce the palladium but as it is oxidized to CO_2 its presence may be detected by passing the gas through $Ba(OH)_2$ after passing through the palladous chloride. (See Brunck, Z. angew, Chem., 25, 2479.) For the blood test for CO see page 295.

Process of Analysis.—Draw into the burette 100 c.c. of the gas and absorb the CO_2 in KOH and the oxygen (some may have leaked into the sample) in the pyro solution. Then run the gas back into the pipette. Carefully measure about 100 c.c. of oxygen, take its temperature and pass it into the combustion pipette. Then carefully draw just one-third of the gas from the pyrogallate pipette into the burette. Pass an electric current through the platinum spiral to heat it to a yellow heat while the top is kept cool by water dripping on the cotton cap and then pass the gas into the pipette carefully so that not more than 10 c.c. passes in per minute. This is best done by entirely closing the tube connecting the leveling bottle with the burette with a screw cock, then setting the leveling bottle up high, then carefully opening the screw cock until the gas is slowly passing into the combustion pipette. The mercury in the leveling bulb of the pipette should be kept about level with that in the pipette to prevent leaks. These are not likely to happen if the rubber connections are reinforced by rubber bands as directed on page 277.

After the gas has all passed over into the pipette, keep the platinum spiral hot for several minutes to insure complete combustion. Then break the circuit, allow the gas to cool a minute or so and run the gas back into the burette. After proper drainage read the volume of the gas and its temperature. Then pass the gas into the KOH pipette and determine the amount of CO_2 produced by the combustion. The methane and ethane are calculated as directed on page 287. Trifling amounts of oxides of nitrogen may be produced by the combustion.

In order to check the result another third of the gas may be taken from the pyrogallate pipette and the combustion repeated. It is necessary to remember that the capillary of the burette holds an appreciable volume and in taking a fraction of a sample in this way this volume must be taken into account. The volume of the capillary may be determined by drawing into the burette some air or gas, reading the volume, then dipping the end of the capillary under water and drawing water into the capillary until it is filled and reading the volume again. The difference is the volume of the capillary.

The combustion pipette should be surrounded with a wire screen to protect the operator in case of an explosion.

It has been assumed that the only hydrocarbons present are methane and ethane. There may be higher hydrocarbons present. These are determined by absorbing them in absolute alcohol. Their solubilities in alcohol are as follows:

1 volume of alcohol dissolves 0.52 volumes of CH_4 at 0°C.
1 volume of alcohol dissolves 1.5 volumes of C_2H_6 at 0°C.
1 volume of alcohol dissolves 6.0 volumes of C_3H_8 at 0°C.
1 volume of alcohol dissolves 18.0 volumes of C_4H_{10} at 0°C.

Pass into the combustion pipette or another one filled with mercury 2 c.c. of absolute alcohol or 1 c.c. of kerosene, then pass in about 100 c.c. of the gas in question and shake it with the gas about a minute. This saturates the alcohol with methane and ethane. Run the gas out of the pipette and the alcohol up in the capillary and then pass into the pipette 100 c.c. of the carefully measured fresh gas. Shake this with the alcohol and then measure the decrease in volume after the gas has stood in the burette long enough for all the alcohol vapors to dissolve in the water.

The decrease in volume is the amount of hydrocarbons higher than ethane. If there is a large amount of these, one treatment with alcohol is not enough. The writer has obtained good results in this way using gas into which had been introduced known amounts of gasoline vapors, petroleum ether vapors, and benzene vapors.

The calorific values of gases may be very accurately calculated from the analysis using the data given in the table on page 327, remembering that the analyses of the gas are always on the dry basis (page 264).

When extreme accuracy is necessary in the analysis of gases by the above methods it is necessary to use somewhat different apparatus, which always involves the use of a compensator attached to the burette and the burette must be graduated to 0.01 c.c. The apparatus shown in Fig. 22 is the one devised by Mr. George Burrell of the Bureau of Mines. For further particulars see J. Eng. Chem., Vol. IV, No. 4.

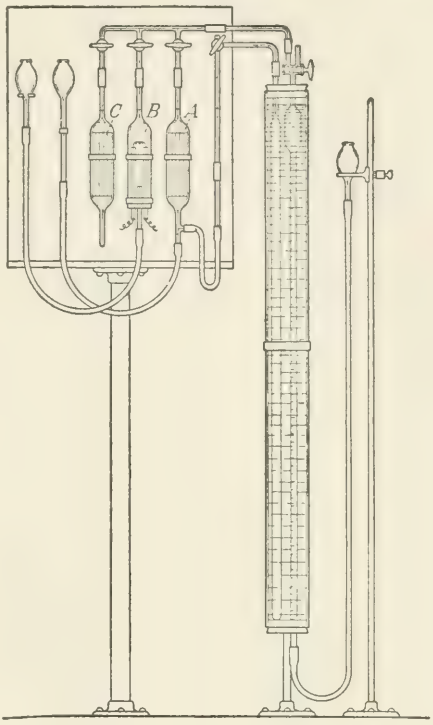

FIG. 22.

THE ANALYSIS OF MINE AIR

This may be done with the above mentioned apparatus of Burrell or Haldane or by the use of the Hesse apparatus here described. The results are very accurate.

The titration method for mine air analysis is especially good on account of the very large sample which can be used and the simplicity of the apparatus.

The CO_2 is determined by absorbing it in a standard $Ba(OH)_2$ solution, the excess of $Ba(OH)_2$ being titrated by a standard oxalic acid solution.

The methane is burned to CO_2 by means of a yellow hot platinum wire, and the CO_2 produced is determined as above indicated.

Solutions Required.—A barium hydroxide solution made by dissolving 15 grams $Ba(OH)_2\ 8H_2O$ and ½ gram of $BaCl_2$ in water and diluting to a liter. The reaction with CO_2 is,

$$Ba(OH)_2+CO_2=BaCO_3+H_2O.$$

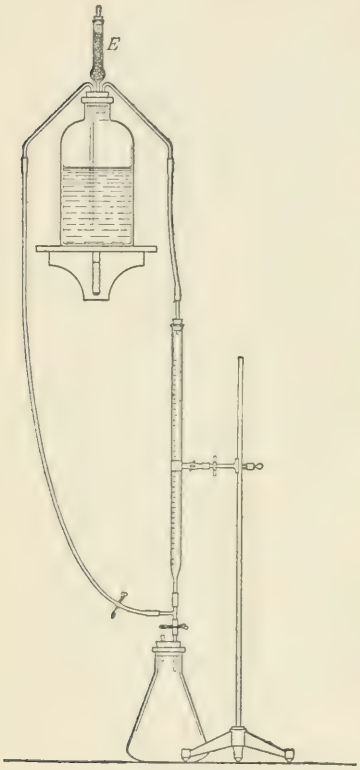

Fig. 23.

One liter of CO_2 at 0°C. and 760 mm. pressure weighs 1.965 grams, and the amount of $Ba(OH)_2$ to be dissolved in a liter is calculated thus, 315.5 : 44 : : X : 1.965. X = 14.09. This would theoretically require 14.09 grams $Ba(OH)_2.8H_2O$ in a liter so that 1 c.c. would equal 1 c.c. of CO_2 at 0°C. and 760 mm. pressure, but the $Ba(OH)_2.8H_2O$ is never pure. The $BaCl_2$ is added to make the end point with phenolphthalein sharp by decreasing the ionization of the BaC_2O_4 formed during the titration.

An oxalic acid solution, 1 c.c. of which equals 1 c.c. CO_2, is used as a standard. Oxalic acid can be obtained pure, it consequently is made of exactly the right strength and the $Ba(OH)_2$ solution is standardized against it. The reaction is $Ba(OH)_2+H_2C_2O_4=BaC_2O_4+2H_2O$. One molecule of oxalic acid is therefore equivalent to one of CO_2 and the amount of oxalic acid required in a liter of solution so that 1 c.c. = 1 c.c. CO_2 is calculated thus (the formula of crystallized oxalic acid being $H_2C_2O_4\ 2H_2O$) 126.04 : 44 : : X : 1.965. X = 5.629. Weigh this amount

carefully, dissolve in CO_2 free distilled water and dilute to a liter with CO_2 free water.

The $Ba(OH)_2$ solution should be kept in a bottle arranged as shown in Fig. 23. In this way the carbon dioxide of the air is kept from the $Ba(OH)_2$. The tube E contains soda lime.

The samples are taken in strong Erlenmeyer flasks of from 500 to 1500 c.c. capacities depending upon the amount of CO_2 and CH_4 in the mine air. The flask is calibrated by filling it with distilled water, forcing a two-holed stopper into it, wiping dry on the outside and weighing. The flask is then emptied, dried and weighed with the stopper. The difference divided by the weight of 1 c.c. of water at the observed temperature of the water is the volume of the flask.

Process of Analysis.—Place in the neck of the dry flask a paper funnel made in the shape of an ordinary glass funnel, extending nearly to the bottom of the flask. Swing the flask and funnel with the funnel mouth turned against the air in the place where the sample is to be taken. The swinging should be done 100 times to remove the air previously in the flask. Then place the two-holed stopper in the flask with plugs in the holes and take the sample to the laboratory.

On reaching the laboratory remove the plugs and insert the tip of the $Ba(OH)_2$ burette which should not fit tightly in the hole. Run in 10 to 20 c.c. of $Ba(OH)_2$ solution, add four drops of phenolphthalein solution and replace the plugs. Shake the flask frequently, and, while the CO_2 is being absorbed, standardize the $Ba(OH)_2$ solution by running into a similar flask filled with pure outdoor air the same amount of $Ba(OH)_2$ solution as was used above and shake both flasks for five minutes, without splashing up on the stopper. Then remove the plugs, insert the tip of a burette through the stopper and run in standard oxalic acid until the phenolphthalein just loses its red color. Do this to both solutions.

Suppose that 20 c.c. of $Ba(OH)_2$ solution were used in each case and that 21 c.c. of oxalic acid were required to standardize the $Ba(OH)_2$. Further suppose that 15 c.c. of oxalic acid were used to titrate the $Ba(OH)_2$ left after absorption of the CO_2 in the sample. Then we have

21 c.c. oxalic acid + CO_2 in pure air = 20 c.c. $Ba(OH)_2$.

15 c.c. oxalic acid + CO_2 in the sample = 20 c.c. $Ba(OH)_2$.

CO_2 in sample = 6 c.c. + CO_2 in pure air.

If the flasks had volumes of 1000 c.c. each and the temperature of the sample was 20°C. and barometric pressure was 745 mm. the percentage of CO_2 in the sample would be,

$(6+0.3) \div (1000-20$ c.c. displaced by $Ba(OH)_2$ solution$) \times {}^{273}\!/_{293} \times {}^{745}\!/_{760} \times 100 = 0.704.$

Pure air contains 0.03 per cent. CO_2.

While the above determination of CO_2 is being made, the methane is determined in another flask whose volume has been determined as above directed with the stopper carrying the electrode in it in the flask (Fig. 24). When the flask is brought to the laboratory the stopper in it is exchanged under pure distilled water for a stopper carrying the electrode made as directed on page 282. The stopper should also have a hole with a glass plug. It is best to stopper the flask at the place of taking the sample with the stopper having the electrode in it, then the exchange of stoppers is eliminated.

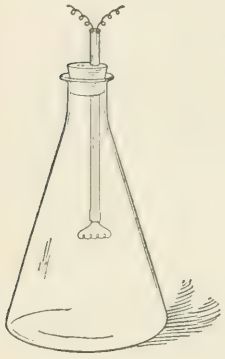

Fig. 24.

Now place the flask with the electrode reaching nearly to the bottom under a stream of water and pass through the platinum wire sufficient electric current to heat it yellow hot and continue the heating at least fifteen minutes. The flask must be kept cool or the air in it will expand and burst it. Now turn off the current and determine the CO_2 in the flask, in exactly the same way as above directed. This includes both the CO_2 produced by the burning of the methane and the CO_2 already in the original sample. From this total is subtracted the CO_2 found in the same volume of the other sample and the difference is the CO_2 produced by the burning of the methane, which is the same as the volume of the methane. This volume is then figured to percentage as directed for CO_2.

Notes on the Process.—It is best to take the samples as above directed rather than by emptying a flask filled with water, for unless the water is very pure distilled water it will cause error by being alkaline or acid, or containing CO_2. Moreover, the flask should not be shipped wet on the

inside if many hours will elapse before the analysis is made for the wet surface of the flask becomes alkaline.

The methane may be determined in the same flask used for the determination of CO_2, after the CO_2 titration.

It is necessary for the platinum spiral to be heated yellow hot or some methane will be unburned.

The water used when the flask is immersed to exchange stoppers *must* be absolutely neutral and free from CO_2 or error will be caused.

References on Gas Analysis:

Bulletin 42 of U. S. Bureau of Mines. Mine Gases and Natural Gas.
Bulletin 19 of U. S. Bureau of Mines. Natural gas.
Bulletin 1 of U. S. Bureau of Mines. Coal gas.
Bulletin 12 of U. S. Bureau of Mines. Furnace gas.
Treadwell-Hall, "Analytical Chemistry," Vol. II.
Winkler-Lunge, "Technical Gas Analysis."
Hempel-Dennis, "Gas Analysis."
White, "Gas and Fuel Analysis."

The Blood Test for CO

With a little experience one can detect as little as 0.03 per cent. CO with the following test: Draw two drops of blood from a finger and dilute to 200 c.c., when the solution should have a buff-yellow tint. Pour the solution in two 100 c.c. tubes. Take one of the tubes into the room, the air of which is to be tested, and allow 50 c.c. of the solution to run out. Stopper the tube and shake the solution gently for 10 minutes, keeping it protected from the light. Then compare the color of the solution with the color of the blood solution in the other tube. If there was more than a trace of CO in the air, the solution with which the air was shaken will have a pink tinge as compared with the color of the other tube.

Iodine Pentoxide Method for CO

The most accurate quantitative method for determining CO in very small amounts is based on the reaction $I_2O_5+5CO=5CO_2+2I$, the CO_2 produced being absorbed in $Ba(OH)_2$ and titrated as above directed. (See Bulletin 42, U. S. Bureau of Mines.)

CHAPTER XXXII

THE ANALYSIS OF CLAYS AND OTHER SILICATES

The methods here given are substantially those given in the United States Geological Survey Bulletin 422. For refined methods see that bulletin. The methods have been adapted to technical use.

Put into a 30 c.c. weighed platinum crucible 1 gram of the finely ground mineral and ignite, carefully at first, and finally to a bright red heat for several minutes. Cool and weigh. Call the loss "loss on ignition." It is chiefly water in the case of clays. Then add 6 grams of pure sodium carbonate, mix the carbonate with the mineral, cover the crucible with a platinum lid and fuse at first cautiously, then at a high temperature over a blast lamp, or a Meker burner, until the fusion is quiet and the mineral decomposed. The blast should be inclined, not directed vertically against the crucible.

Remove the cover, seize the crucible in the tongs, and allow the melt to solidify while the crucible is kept tipped on its side so that the contents will solidify in a thin sheet on the side of the crucible and can be easily removed. To remove the cake gently press the sides of the crucible, when the cake will crumble to pieces. Transfer the contents of the crucible to a casserole, or better, to a silica dish, dissolve what remains in the crucible, and what spattered on the lid, with hot water and transfer the solution to the casserole. Add 100 c.c. of hot water to the casserole, heat until the cake is all decomposed and no hard lumps remain. Then add 15 c.c. of HCl gradually with a cover-glass on the casserole in order to prevent loss by frothing, wash out the crucible with a little HCl and add the solution to the casserole. Set the casserole on a hot plate or steam-bath and evaporate to hard dryness. An air blast over the surface will greatly hasten the evaporation.

Pour over the dry mass 30 c.c. of 1:1 HCl and heat almost to boiling for several minutes, then add 50 c.c. of hot water, boil

several minutes and filter the solution through an ashless filter. Transfer as much of the silica to the filter as is convenient but do not try to remove the last trace. Wash the silica until no test for chlorine is obtained (while the filtrate is evaporating). Add the washings and evaporate the entire filtrate to dryness, dissolve as before and filter through another paper, and transfer all silica obtained the second time (about 1 per cent. of the silica in the sample) to the paper. This necessitates vigorous use of a policeman. Wash the paper free from chlorine, place the two papers and their contents in a platinum crucible, very carefully drive off the water and burn off the paper. When the paper is burned off, cover the crucible with a lid and ignite the silica at a high temperature with a blast lamp or Meker burner for at least 15 minutes, for this long blasting is necessary to drive off the last trace of water. Cool and weigh the crucible and contents. Then moisten the silica with water, add a few drops of sulfuric acid and 10 c.c. of HF. Evaporate off the HF on a hot plate, *in a good hood,* then raise the temperature and drive off the sulfuric acid and finally ignite the crucible to a bright red heat, cool and weigh. The loss in weight is the silica.

Add a few cubic centimeters of HCl to the crucible and loosen the residue, consisting chiefly of titania, alumina, and oxides of iron and phosphorus, by rubbing the bottom with a policeman. The residue loosens easily. Pour the solution into the filtrate from the silica.

To the filtrate from the silica having a volume of about 250 c.c., add a 11-cm. filter paper thoroughly macerated by shaking it violently in a flask with 25 c.c. of water, then add NH_4OH until nearly neutralized, heat to boiling and add NH_4OH until just barely alkaline, boil for a minute or so and filter (preferably using suction.) Wash the precipitate two or three times with water, then wash it back into the beaker in which the precipitation was made, dissolve it in 15 c.c. HCl, dilute the solution to 100 c.c., heat to boiling and precipitate with NH_4OH as before. It is important that the solution be made only barely alkaline otherwise manganese will precipitate partially. Filter through the same paper as before, wash with 5 per cent., NH_4NO_3 solution until free from chlorine, dry the precipitate of $Fe(OH)_2$, $Al(OH)_3$, $Ti(OH)_4$, P_2O_5, a little SiO_2, etc., in a weighed platinum crucible,

burn off the paper at a low temperature, then ignite the precipitate over the blast lamp or Meker burner for 15 minutes with an oblique flame, if a blast is used. Cool in a desiccator and weigh quickly with a lid on the crucible, for the precipitate takes up moisture from the air easily after having been ignited in the presence of macerated paper.

Transfer the precipitate to a small beaker, add 10 c.c. of HCl and 10 c.c. of 1 : 1 H_2SO_4 and evaporate until the H_2SO_4 fumes strongly to render insoluble the few milligrams of SiO_2 always present, cool, add 20 c.c. of water and heat until everything but the SiO_2 is in solution. Filter off the SiO_2, wash it, ignite and weigh. Treat with a few drops of H_2SO_4 and 1 c.c. of HF, evaporate, ignite and weigh. Add this SiO_2 to that previously obtained. It may possibly contain some $BaSO_4$. This method for dissolving the ignited oxides is excellent when they have been precipitated with macerated filter paper.

In the filtrate determine the iron and titania. Determine the iron preferably as follows: dilute the solution to 200 c.c. in a small flask with a two-hole stopper, heat to boiling, pass through a stream of H_2S till the iron is reduced, cool, filter off the sulfur and platinum sulfide, again pass a stream of H_2S and then continue the boiling while a stream of CO_2 is passed through until the issuing gas does not blacken a piece of filter paper moistened with lead acetate. Cool while the CO_2 continues to pass and then titrate with a permanganate solution. If titanium is low the iron may be determined by the zinc-permanganate method. After the iron is titrated determine the titanium by adding H_2O_2 and determining the titanium colorimetrically as directed on page 167. If it is suspected that the precipitate of $Al(OH)_3$, etc., contained some manganese, divide the solution of the sulfates in two equal parts, and in one determine the iron and titanium and in the other determine the manganese by the bismuthate method.

Subtract the weight of the Fe_2O_3, TiO_2, SiO_2 and P_2O_5 from the weight of the ignited precipitate to get the weight of the Al_2O_3. The P_2O_5 must be determined in a separate sample as directed for iron ores.

The filtrate from the $Al(OH)_3$, etc., contains practically all the manganese, calcium, magnesium, strontium, barium, and possibly traces of other elements.

If there is any manganese, zinc, cobalt, nickel, copper, etc.,

present, add to the hot solution 3 c.c. of NH_4OH and about the same amount of ammonium sulfide, shake well and filter off the sulfides. Determine the manganese, if it is desired, in the sulfides by the bismuthate method exactly as if the precipitate were a steel. Or the manganese may be precipitated later on with the magnesium and determined then.

Evaporate the solution if necessary to 300 c.c., heat to boiling and precipitate the calcium and strontium by adding a sufficient amount of ammonium oxalate (10 c.c. or more of saturated solution). The precipitate, if small, should be allowed to settle several hours. Filter it off on a close paper, dry and ignite the oxalate to calcium oxide by ignition in a platinum crucible over a blast for several minutes. Cool in a desiccator and weigh. If the precipitate is large, it must be dissolved and reprecipitated.

In the filtrate from the calcium, precipitate the magnesium with sodium phosphate, allow to settle over night if possible, filter on a weighed Gooch crucible, ignite and weigh as $Mg_2P_2O_7$. If manganese is present, determine it in the precipitate by the bismuthate method.

Feldspars often contain barium. This may be detected by making the filtrate from the magnesia acid with sulfuric acid and precipitating the barium as barium sulfate.

Determination of the Alkalies by J. Lawrence Smith Method

When silicates containing K_2O and Na_2O are heated with a mixture of $CaCO_3$ and NH_4Cl, $CaCl_2$ is first formed by double decomposition, and this then acts on the silicates forming alkaline chlorides and lime silicates. A red heat is necessary.

There is needed, first, pure $CaCO_3$ free from K_2O and Na_2O. This can be prepared by dissolving marble in HCl, to saturation, adding a little slaked lime to make the liquid alkaline and precipitate Fe_2O_3, Al_2O_3 and P_2O_5, then diluting and heating the liquid and precipitating the $CaCO_3$ by $(NH_4)_2CO_3$. This is washed till free from HCl and dried. The other substance needed is pure NH_4Cl. This must be powdered and must volatilize without residue at a low red heat.

Process of Analysis.—Mix 1 gram of clay with 1 gram of NH_4Cl. Grind them together in a small porcelain mortar. Add 8 grams of $CaCO_3$ and mix thoroughly with the clay and NH_4Cl.

Put a little pure $CaCO_3$ on the bottom of a large (30 to 50 c.c.) platinum crucible and then add the mixture. Clean out the mortar by grinding a little more $CaCO_3$ in it and add this on top of the mixture as a cover. Place the crucible three-fourths through a hole in an asbestos board in which the crucible tightly fits, cover the crucible with its lid and set on the lid a large porcelain crucible filled with water. This keeps the top cool and prevents loss of vapor of the alkalies.

Now heat carefully, gently at first, with a Bunsen flame about an inch long just touching the crucible, as long as an odor of ammonia is given off. Then heat to full redness for three-fourths of an hour with a Meker burner. Cool and transfer the sintered mass to a casserole. Wash the crucible and cover with hot water and add the washings. Digest the whole until the mass slakes to a fine powder. Now filter and wash with hot water until the filtrate amounts to 250 c.c.

This amount of washing will take out all the alkali, though the filtrate will still react for chlorine, due to the fact that the CaO retains slowly soluble oxychlorides which it is impossible to wash out completely, and which will cause the filtrate to react for chlorine indefinitely.

To the hot filtrate add NH_4OH and $(NH_4)_2CO_3$ in excess. The calcium separates as carbonate, which on heating becomes granular and easily filtered. Filter and wash with water containing a very little NH_4OH.

Concentrate the filtrate to small volume in a large silica or platinum dish, then transfer it to a small dish and finally evaporate it to dryness. Now ignite it carefully at a heat not exceeding a barely visible red, until all NH_4Cl is expelled and no more fumes form. Cool, add a little water and a drop of $BaCl_2$, then a cubic centimeter of 10 per cent. $(NH_4)_2CO_3$ and a cubic centimeter of $(NH_4)_2C_2O_4$, heat and filter from any residue. Add two or three drops of HCl to the filtrate and again evaporate to dryness in a weighed dish. Dry, ignite carefully as before and weigh as KCl+NaCl. The chlorides must be *white* and dissolve without residue in water. If there be a residue, weigh it.

To the water solution, about 10 c.c. in volume, add an excess of platinic chloride, and evaporate carefully until only a drop of liquid is left. Add 20 c.c. of alcohol (80 per cent.) and

let stand till the platinum salts dissolve. Filter onto a weighed Gooch filter. Wash the K_2PtCl_6 with 80 per cent. alcohol. Dry and weigh. Calculate the K_2O from the weight of this and the Na_2O from the remainder, after deducting the KCl, calculated from the K_2O, from the mixed chlorides.

The strength of the alcohol is important. The K_2PtCl_6 is practically insoluble in 80 per cent. alcohol, but the Na_2PtCl_6 will dissolve in it. Time must be given to secure complete solution of this latter salt.

Notes on Silicate Analysis.—The above methods are quite accurate and for technical purposes may sometimes be shortened. There are, however, some small errors to be corrected for in exact work.

The loss on ignition includes hygroscopic water, combined water, carbon dioxide from carbonates, organic matter, sulfur, oxygen from MnO_2, while the sample may take up oxygen by oxidation of ferrous iron, etc. For a full discussion see U. S. G. S. Bulletin 422.

When evaporations are made in porcelain casseroles and precipitations in glass beakers a milligram or two of SiO_2 and Al_2O_3, etc., will be obtained from them. To get exact results a blank must be run.

If the sample contains fluorine some silica will be lost as tetrafluoride.

The precipitate of iron, aluminium, and titanium hydroxides will generally be contaminated with a small amount of manganese, always with one or more milligrams of silica, all the phosphorus in the sample, vanadium if it be present, chromium, zirconium, etc. For exact work these must be determined in the precipitate. Sometimes a sample of clay or slag may have several per cent. of P_2O_5 which should be determined as in an iron ore.

The use of macerated filter paper makes the filtration of a large precipitate of $Al(OH)_3$ much easier and also greatly aids the subsequent solution of the ignited precipitate. In fact it is generally soluble in 1:2 sulfuric acid.

When iron is reduced there should be not more than 2 or 3 per cent. of sulfuric acid present.

The precipitate of $Al(OH)_3$, etc., must be washed with an ammonium salt, not pure water. Clays always contain at least traces of titania.

The precipitate of calcium oxalate is generally contaminated with a small amount of aluminium hydroxide, iron hydroxide, magnesia, sodium and strontium. To remove these (except strontium) the precipitate is ignited, dissolved in HCl, made alkaline with ammonia, boiled, aluminium filtered off and the calcium precipitated again.

The precipitate of magnesium phosphate is likewise apt to be con-

taminated with barium, calcium, manganese, alumina, etc., and unless two precipitations are made the precipitate is apt to contain too much ammonium phosphate and be too heavy. Manganese may be determined colorimetrically in the precipitate.

In the alkali determination especial care must be taken to make sure that the heat is not so high at first as to drive off the ammonium chloride instead of breaking it up to form $CaCl_2$ and ammonia.

Analysis of Blast-furnace Slags

The slags made in the iron blast furnace are essentially silicates of lime, magnesia and alumina. They usually contain, however, small percentages of iron, manganese, and sulfur. Phosphorus is rarely present in more than traces. Titanium and other rarer elements, if present in the ore, will be found in the slag. Slags that are high in alumina and magnesia, will sometimes contain small crystals of spinel ($MgOAl_2O_3$). As this substance is neither attacked by HCl, decomposed by fusion with Na_2CO_3, nor dissolved by HF, it will be found in the silica obtained in the analysis. Spinel can be decomposed by prolonged treatment with hot H_2SO_4 diluted with its own volume of water.

Most furnace slags can be decomposed by treatment with HCl, especially if they have been suddenly cooled from the molten state. Slags that are not decomposed by HCl must be fused with Na_2CO_3.

Slags frequently contain metallic iron in small grains; this should be taken out of the crushed sample by a magnet. If the slag itself is magnetic the metal grains can be picked out under a magnifying glass with pincers. The sample must finally be ground in an agate mortar to an impalpable powder.

The exact analysis of slags is carried out the same as the analysis of silicates, as given above. If the slag has much manganese the first precipitation of alumina and ferric hydroxide must be made by the basic acetate method, otherwise they will retain considerable manganese.

If the slag is soluble in HCl, the fusion with sodium carbonate is unnecessary.

Short Method.—For the purpose of furnace control, it is usually sufficient to know the percentages of silica, alumina, lime and magnesia in a slag. These can be determined with sufficient accuracy by the following process.

The Determination of the CaO and the MgO.—Weigh 1 gram of the sample into a casserole, add 30 c.c. of water and stir the slag up into it to prevent caking and the separation of gelatinous

silica on the addition of acid. Now add 20 c.c. of HCl and heat. Everything should dissolve except a few flakes of SiO_2 and possibly a little carbon or sulphur. There should be no gritty residue. Cover the casserole, and boil the solution to dryness to separate most of the silica.

Now add 10 c.c. of HCl, a few drops of HNO_3, and then 50 c.c. of water. Boil to dissolve the bases and then transfer the contents of the casserole, without filtering, to a 500 c.c. graduated flask. Dilute the liquid to about 300 c.c. and add NH_4OH until the alumina separates, but avoid a large excess. If the sample contains more than a few tenths per cent. of manganese, add 2 or 3 c.c. of ammonium sulfide to precipitate it with the alumina. Heat the contents of the flask to boiling and boil for three minutes. Cool the liquid and dilute it to the mark with water free from CO_2. Mix the contents of the flask thoroughly and then filter off 250 c.c. through a dry filter.

Determine the lime and magnesia in this volumetrically as in a limestone. If ammonium sulfide was used, add HCl to the filtered solution, till it is neutral and then about 5 c.c. in excess. Boil till the H_2S is expelled, then add 0.5 gram of $KClO_3$ and heat till the separated sulfur is dissolved. Now add NH_4OH in excess and proceed with the determination of the lime as before. Should a trace of MnO_2 separate on adding the ammonium hydroxide, continue the heating till it dissolves and the solution is nearly colorless, before precipitating the lime.

The Determination of the SiO_2 and the Al_2O_3.—Weigh 0.5 gram of the sample into a casserole, treat it with water and HCl and evaporate to dryness as before, in this case, however, the dry residue must be heated till all HCl is expelled, avoiding a temperature of over 120°.

Take up the residue in water and HCl, filter and weigh the silica. It is well to evaporate the solution to dryness a second time before filtering off the silica, as this makes the filtration more rapid.

The residue is usually taken to be silica but is liable to contain traces of Fe_2O_3, TiO_2, and spinel. It may be tested with HF and any fixed residue deducted. (See page 298.) If this is done, the silica should be separated by a double evaporation as it is not all precipitated by a single one. Ordinarily the

impurities present will about balance the silica lost and so the gross weight is nearly correct.

The alumina is now determined in the filtrate from the silica.

In the absence of much manganese this can be done by precipitation with NH_4OH as in the analysis of a limestone, taking care to have plenty of NH_4Cl present and to redissolve the first precipitate which is likely to contain a little lime. The precipitate should be washed by decantation until free from chlorides and then transferred to the filter. The precipitate contains all iron, phosphoric acid and titanic acid in the slag.

If the slag contains much manganese, the alumina must be separated from it by a basic acetate precipitation as described on page 73. The precipitate is then redissolved in HCl and the alumina, now free from manganese, precipitated with NH_4OH.

Determination of Al_2O_3 as Phosphate.—Dilute the filtrate from the silica in a 300 c.c. beaker to about 200 c.c. To the cold solution add about 15 c.c. of a saturated solution of sodium phosphate, and then NH_4OH cautiously and with constant stirring until a slight permanent precipitate forms. Now add 5 drops of HCl which should dissolve the precipitate and leave a clear solution. Then add with constant stirring 20 c.c. of a saturated solution of sodium thiosulfate. If much iron is present as in the case of an ore, the solution will turn nearly black, but on continuing the stirring will grow lighter as the iron is reduced and finally a white precipitate of $AlPO_4+Ti_3(PO_4)_4$ will be thrown down mixed with a large quantity of S. Cover the beaker and heat the solution till it boils. When boiling add 20 c.c. of a solution consisting of 100 grams of sodium acetate, 200 c.c. of acetic acid, sp. gr. 1.04, and water to make 500 c.c. Boil the solution 10 minutes longer or till the precipitate coagulates.

Let the precipitate settle, filter, and wash the precipitate ten times with hot water. Put the wet filter into a crucible, ignite at a low heat to burn off the paper and sulfur, and then ignite over the blast lamp.

The residue is $AlPO_4+Ti_3(PO_4)_4$ and contains 0.418 Al_2O_3 if Ti is absent.

REFERENCE:

J. M. CAMP, *Iron Age*, LXV, 17.

When this method is applied to ores the first precipitate is likely to contain a little iron. This can be removed by dissolving and reprecipitating it in the same way.

Sulfur and iron can be determined in slags as in iron ores.

Sulfur.—The sulfur in slags is present almost wholly as calcium sulfide. It can be determined approximately by adding 150 c.c. of water to 0.5 gram of the very finely pulverized slag and titrating with the standard iodine solution used for sulfur in iron.

Stir the mixture of slag and water and add 3 or 4 c.c. of starch solution, then run in the iodine till the blue color develops. Now add 15 c.c. of concentrated HCl, stir and add the iodine again until the color no longer disappears.

If 1 c.c. of the iodine equals 0.0005 gram S, each cubic centimeter taken will be equivalent to 0.1 per cent. sulfur in the slag.

Reference:

J. Anal. and App. Chem., Vol. VII, No. 5.

It is probably more accurate to evolve the H_2S in a flask as for pig-iron. Put 5 grams of granular zinc into the flask, then add 0.25 to 0.5 gram of the very finely ground slag. The hydrogen from the Zn carries over the H_2S from the slag. This is absorbed by an ammoniacal cadmium solution and titrated as usual. See Camp, "Methods of Analysis in the Laboratories around Pittsburg," 2nd ed., p. 147.

Manganese in slag can be determined as in iron ores. Small percentages are best estimated by the bismuthate method.

Mineral Analysis of Clays

This is sometimes very useful. It depends upon the fact that kaolin is soluble in sulfuric acid with the liberation of silica soluble in NaOH, while quartz and feldspars are not appreciably soluble in either of the above reagents unless extremely finely ground.

Process of Analysis.—Place 2 grams of the clay in a 250 c.c. flask and add 100 c.c. of water and 20 c.c. of strong sulfuric acid. Boil down the solution until the acid fumes strongly. Cool, add 50 c.c. of water, heat until the $Al_2(SO_4)_3$ is all in solution and filter through a double filter. Wash well with water, wash the residue back into the flask and add 50 c.c. of a 7 per cent. sodium

hydroxide solution, heat to boiling for five minutes, and filter through the same paper without transferring the residue thereto. Again add 50 c.c. of 7 per cent. soda, heat to boiling and shake the solution, transfer the residue to the paper, filter, wash well with water, then with dilute HCl, ignite and weigh. The decrease in weight is "clay substance." Fuse the residue with sodium carbonate, and determine the silica in it. This subtracted from the weight of the clay-free residue gives the alumina and alkalies in the feldspars, which multiplied by 3 gives the amount of feldspar present; for the alumina and alkalies in the common feldspars will average about one-third of them. The sum of the clay substance and feldspars subtracted from 100 will give the quartz in the sample.

The results are only approximate and the method does not apply to red clays or clays containing limestone.

Determination of Silica, Alumina, Lime and Magnesia in Iron Ores

Silica.—Put 2 grams of the ore in a 12-cm. porcelain dish with cover; add 30 c.c. of strong hydrochloric acid, and heat for half an hour or until the action of the acid has ceased, but do not allow the acid to boil. Cool the solution for a few minutes; dilute to twice the volume with hot water, and filter into another dish. Wash the residue with hot water until the water runs through colorless; ignite the filter and residue in a platinum crucible, and fuse the impure silica with about five times its own weight of Na_2CO_3. When the fusion has become tranquil place in it a stout piece of platinum wire about 8 cm. long, with the end that is put into the crucible flattened and bent at right angle; incline the crucible slightly, then remove the heat, and hold the wire in position, touching the bottom of the crucible, until the mass solidifies. Now heat the crucible rapidly and uniformly with the blast-lamp or Bunsen burner; lift out the melt with the wire as soon as it is loose, and place it in the dish in which the ore was first treated. Cover the dish, add about 30 c.c. of hot water to disintegrate the fusion, then add hot water to the crucible and dislodge adhering substance as completely as possible with a glass rod. Add the washings from the crucible to the main portion in

the dish, and acidify the whole with 15 c.c. of strong hydrochloric acid. Cleanse the crucible thoroughly by warming a little hydrochloric acid in it, and when the solid matter is completely disintegrated, scrub the crucible with a policeman, and rinse again. Evaporate the solutions in both dishes to dryness, and continue to heat for an hour at about 120°C. Add to the dish containing most of the iron 15 c.c. of strong hydrochloric acid, and warm until the ferric oxide is dissolved. To the other dish, containing most of the silica, add just enough dilute hydrochloric acid to moisten the residue and warm, then add about 30 c.c. of hot water and boil. Pour the solution from this dish into the other dish, keeping back most of the silica, filter the contents of both dishes into a 200 c.c. graduated flask, wash both dishes carefully, using a rubber-tipped rod to remove adhering matter, and wash the filter free from chlorides. Set aside the filtrate for the determination of alumina, etc. Ignite the residue, and weigh as impure SiO_2. Add two drops of sulfuric acid, 10 c.c. of HF, evaporate to dryness, ignite and weigh. The loss is SiO_2.

For exact results two evaporations to dryness are necessary. Otherwise the SiO_2 will be slightly low.

Clean the residue out of the crucible with a few cubic centimeters of HCl using a policeman, and add the solution to the filtrate from the SiO_2.

Alumina.—The aluminium and iron are first separated from the manganese and other bases by the basic acetate precipitation; the resulting hydroxides are dissolved with hydrochloric acid, and the aluminium is separated from the solution as phosphate. Having cooled the filtrate from the silica in the flask and made the solution up to the mark, transfer one-half of the solution to a 600 c.c. beaker. Add 10 c.c. of strong hydrochloric acid; heat to boiling, cool, add NH_4OH until a very slight, permanent precipitate forms, while the solutions remain slightly acid, then add 25 c.c. of 20 per cent. ammonium acetate solution; dilute to about 450 c.c. with hot water; boil for one minute, and allow to stand until the precipitate settles. While heating the liquid, stir it frequently to prevent "bumping," and turn down the flame as it begins to boil. When the precipitate has settled, decant and filter the liquid through a 10-cm. ribbed funnel with the paper cut to fit. Rinse the beaker once,

and wash the precipitate three times with hot water. Save the filtrate for the determination of manganese, etc. Place the beaker in which the precipitation was made under the filter, and dissolve the precipitate with hot hydrochloric acid (1 : 1) and wash with hot water, making up the volume of the solution to about 300 c.c. Add to the solution 30 c.c. of saturated ammonium phosphate, then add NH_4OH until a slight precipitate appears, and dissolve this with a few drops of hydrochloric acid. Now add to the clear solution 50 c.c. of 10 per cent. sodium thiosulfate solution; stir until a white precipitate forms, place the beaker over a flame, and just before the liquid begins to boil add 12 c.c. of ammonium acetate and 8 c.c. of strong acetic acid. After boiling for 10 minutes, filter the liquid rapidly, keeping the precipitate covered with the liquid. Wash the filter and precipitate with hot water until free from chlorides; ignite in a porcelain crucible, and weigh as $AlPO_4$. Titania if in the ore will contaminate the $AlPO_4$. Two precipitations are necessary for the best results.

Manganese.—From the filtrate from the basic acetate separation of the iron and aluminium, precipitate the manganese as directed under the acetate method for manganese. If the precipitate is small, it should be washed well and the manganese determined in it by the bismuthate method.

With ores containing as much as 2 per cent. of manganese a double precipitation of iron and aluminium hydroxides should be made.

Lime and Magnesia.—Concentrate the filtrate from the manganese determination to half its volume, add 15 c.c. of ammonium oxalate solution, and NH_4OH until alkaline, and heat just below the boiling-point until the precipitate settles readily. If there is no immediate precipitation, concentrate the solution to about 100 c.c., before adding the NH_4OH; boil for 15 minutes and filter. Wash the precipitate free from chlorides, ignite to constant weight with the blast-lamp, and weigh as CaO.

Cool the above filtrate; precipitate the magnesia by adding 10 c.c. of sodium phosphate solution and 10 c.c. of NH_4OH, stir well, and set aside for 12 hours. Filter on a 9-cm. paper; wash with the ammonia and ammonium nitrate solution; ignite at the

lowest temperature necessary to burn off the paper, and weigh as $Mg_2P_2O_7$.

If an accident happens to any of the above determinations use the other half of the filtrate from the silica for another analysis.

Phenylhydrazine Method for Alumina

The alumina may be determined as follows: Dissolve several grams of the ore in HCl and filter, ignite the residue, decompose it with HF, evaporate to dryness with a drop of H_2SO_4, dissolve in HCl and add to the main solution. Dilute to 250 c.c., nearly neutralize, and reduce the iron with NH_4HSO_3. If the solution turns deep red (ferric sulphite), it is not acid enough, and a few drops of hydrochloric acid should be added, for the sulphite itself does not reduce ferric salts, at least not with rapidity. Now quickly bring to neutrality with ammonia, and then add several drops of dilute hydrochloric acid. If this last operation is done too slowly the oxygen of the air helps to form a little ferric hydroxide which does not always readily dissolve in the dilute acid. Finally, add from 1 to 3 c.c. of phenylhydrazine, according to the weight of the alumina to be precipitated. If too little has been used, a few drops added to the filtrate will disclose the mistake. Stir until the precipitate has become sufficiently flaky and allow to settle. The supernatant liquid will now be plainly acid to litmus. One need not be disturbed if the precipitate has a brownish color, for it is not due to ferric hydroxide, but to the coloring matter contained in all phenylhydrazine which has not been freshly distilled. When the determinations are allowed to stand too long the air increases this oxidation product, and a brown insoluble scum forms on the surface of the liquid and on the sides of the vessel, which is rather troublesome to the analyst. Fortunately equilibrium appears to be established in a short time. The vessels need not stand more than an hour, at any rate. The precipitate is washed by a solution of phenylhydrazine sulphite made by adding cold saturated sulphurous acid to a little phenylhydrazine until the crystalline sulphite first formed dissolves in the excess. The solution has an acid reaction. Five to 10 c.c. of this are used in 100 c.c. of hot water.

Ignite the precipitate and weigh the Al_2O_3, TiO_2, P_2O_5 and V_2O_4 if present. Determine the TiO_2, P_2O_5 and V_2O_4 and obtain the Al_2O_3 by difference.

CHAPTER XXXIII

SOFTENING WATER FOR BOILER USE

The scale-forming materials in water are $CaH_2(CO_3)_2$, $MgH_2(CO_3)_2$, $CaSO_4$, $MgSO_4$, $CaCl_2$, $MgCl_2$, $Fe_2(SO_4)_3$, SiO_2, $Al_2(SO_4)_3$, and other salts. The most common compounds which give trouble in boilers by causing scale are the first four given above, except in the case of mine water when sulfates of iron and alumina are frequently present.

Water is softened by adding lime (CaO) and soda ash (Na_2CO_3). The reactions are:

$$CaH_2(CO_3)_2+CaO=2CaCO_3+H_2O.$$
$$MgH_2(CO_3)_2+2CaO=Mg(OH)_2+2CaCO_3.$$
$$MgSO_4+CaO+H_2O=CaSO_4+Mg(OH)_2.$$
$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

To determine the amount of lime and soda ash to add to soften the water proceed as follows:

Put in a 250 c.c. Jena flask 200 c.c. of the water to be tested, add 50 c.c. of saturated lime water and heat to boiling. Cool, shake well and filter through a rapid filter, wash three times with pure, freshly boiled water, and titrate the filtrate with N/28 HCl, using methyl orange as indicator. Treat 200 c.c. of freshly boiled distilled water in exactly the same way, being careful to use the same amount of methyl orange in both cases and to finish at the same depth of color. The number of cubic centimeters of standard HCl used the second time, minus the number of cubic centimeters used the first time, multiplied by 5 gives the parts of lime to add to a million parts of water.

Now add to the titrated water in a porcelain dish 30 c.c. of N/14 Na_2CO_3, heat to boiling, cool, filter and titrate the excess of soda. The sodium carbonate precipitates both the $CaCl_2$ made in the first titration and the $CaSO_4$, etc., in the water. Therefore, to calculate the amount of sodium carbonate necessary to soften the water subtract from $2\times30=60$, the total amount of N/28 HCl that has been used in both titrations and multiply by 9.45.

To determine the amount of carbonate or "temporary" hardness in water, it is only necessary to titrate it with a standard acid with methyl-orange indicator. The carbonate hardness is due to the bicarbonates of calcium and magnesium, $CaH_2(CO_3)_2$ and $MgH_2(CO_3)_2$, which are alkaline to methyl orange because they are salts of strong bases and a very weak acid and hydrolize, thus,

$$CaH_2(CO_3)_2+2HOH=Ca(OH)_2+2H_2CO_3.$$

To make the titration, place 100 c.c. of the water in each of two Nessler tubes, add to each five drops of methyl-orange solution and titrate the water in one of the tubes until it has a slight reddish color when compared with the color in the other tube. The reaction is $CaH_2(CO_3)_2+2HCl=CaCl_2+2H_2CO_3$ and similarly for the magnesium salt. The cubic centimeters of standard HCl multiplied by its normality and by 50 gives the results in milligrams of carbonates present figured as $CaCO_3$. Thus if 5 c.c. of N/10 HCl were used, the result would be $5\times0.10\times50=25$ mg. of $CaCO_3$ per 100 c.c. or 250 parts of $CaCO_3$ per million of water.

To determine the sulfate or "permanent" hardness, evaporate 100 c.c. to hard dryness in a platinum, or silica, or nickel dish (not in a glass vessel) with 25 c.c. of N/10 Na_2CO_3, dissolve the excess of Na_2CO_3 in pure distilled water, filter and wash the paper well. Titrate the filtrate in a Nessler tube as directed for the titration of temporary hardness with the standard acid, using methyl-orange indicator. The cubic centimeters of N/10 soda consumed multiplied by 6.8 gives the permanent hardness in terms of milligrams of $CaSO_4$ present. This multiplied by 10 gives the parts per million. Instead of boiling to dryness with sodium carbonate, it is quicker and accurate to simply boil a few minutes with a mixture of equal parts of N/10 sodium carbonate and sodium hydroxide, filter and titrate.

References:

Drawe, *Z. angew. Chem.*, XXIII, 52.

Proctor, *J. Soc. Chem. Ind.*, Jan. 15, 1904.

Methyl-orange Solution.—Dissolve 0.025 gram of the sodium salt in 100 c.c. of water and add 0.7 c.c. of N/10 HCl.

In the examination of a new supply of water for boiler purposes it is safest to make a complete analysis in addition to the above softening tests.

Outline Process for the Analysis.—First, evaporate 100 c.c. of the clear water (filtered if necessary) to dryness in a weighed platinum dish, and dry at 100° to constant weight. This gives the "total solids." After weighing the dish ignite it very cautiously, not passing a barely visible red heat, until the residue becomes nearly white. Weigh again after cooling in a desiccator. The loss is water of combination and organic matter, and the residue is the fixed mineral matter.

Second, test the water for chlorine.[1] If it contains more than a trace, the amount may be determined by titrating 100 c.c. of the water with a standard solution of $AgNO_3$, adding a little neutral potassium chromate to serve as an indicator. A slight excess of $AgNO_3$ gives the reddish color of silver chromate.

The small excess of the silver solution required to give the red color that forms the end reaction can be determined by adding 1 c.c. of a standard solution of NaCl (1 c.c. equals 1 mg. Cl) to 100 c.c. of distilled water, and titrating this in the same way. The excess of the silver solution over that required for the chlorine present is the amount that must be deducted from that used in the regular titration.

Third, acidulate 1 liter with 5 c.c. HCl, evaporate to dryness in a platinum dish, adding it to the dish a little at a time. Take up the residue with HCl and water, and determine the SiO_2, Fe_2O_3 and Al_2O_3, CaO and MgO exactly as in the case of limestone. In filtering off the SiO_2 care must be taken that no $CaSO_4$ (which is frequently present in considerable quantity) be left undissolved with the SiO_2. It can all be dissolved with water and HCl.

For ordinary work where the amount of SiO_2 is usually very trifling and of no technical importance, the evaporation to dryness can be omitted. In this case evaporate 1 liter of the water with 5 c.c. of HCl in a large beaker, to about 100 c.c. Add an excess of NH_4OH and filter from the precipitate of $Fe(OH)_3$, $Al(OH)_3$ and SiO_2. Care must be taken to have enough NH_4Cl

[1] See Fresenius, "Quantitative Analysis."
Mellor, "Quantitative Inorganic Analyses" (1913).

present to prevent any precipitation of the magnesia. The CaO and MgO are determined in the filtrate as before.

Fourth, acidulate 500 c.c. of the water with 1 c.c. of HCl and evaporate to 100 c.c. Filter if necessary and determine the SO_3 by precipitation with $BaCl_2$.

The alkalies may be determined closely enough for technical purposes by difference as follows:

Evaporate 100 c.c. to dryness with a slight excess of H_2SO_4 in a weighed platinum dish. Ignite the residue cautiously till the fumes of H_2SO_4 are all driven off; do not exceed a low red heat. Now put a few small pieces of pure $(NH_4)_2CO_3$ into the dish, and cautiously heat till it is evaporated. This will expel the acid retained by the alkalies, to form bisulfates. Avoid too much heat or $MgSO_4$ will be decomposed. Now cool and weigh the dish which contains the sulfates of all the bases in the original water. Calculate the CaO and MgO as sulfates, add the Fe_2O_3, Al_2O_3 and SiO_2, and deduct the sum from the weight of the sulfates in the dish. The difference may be taken as sodium sulfate.

If a more exact determination of the alkalies is needed, evaporate 1 or 2 liters of the water to dryness in a platinum dish. Glass is liable to give up alkali. Extract the residue with water, add an excess of pure milk of lime, digest and filter, and proceed with the solution as with the filtrate from the lime in the determination of alkalies in the analysis of fire clay. A blank must be run on all the reagents. In place of using a platinum dish the water may be boiled down to dryness in a clean tin sauce pan, and the residue used for the determination of the alkalies. This will be found a useful method where a number of waters are to be analyzed and the supply of platinum ware is short.

Calculation of the Results.—In stating the results of the analysis it is customary to combine the acids and the bases in the following manner: The alkalies are first combined with the chlorine, any excess being then combined with the sulfuric acid. Should there be more chlorine than will combine with the alkalies the excess is calculated first to the calcium and when that is used up, to the magnesium. Should there be alkalies more than sufficient to saturate both the chlorine and the sulfuric acid the excess is estimated as carbonate.

The sulfuric acid left after the alkalies are satisfied is then united with the calcium and any excess combined with the magnesium.

All the calcium and magnesium not required for the chlorine and the sulfuric acid are then calculated as carbonates.

This order can be departed from where there is evidence of some other combination. In water that has been treated with lime and soda to remove the lime, magnesia is frequently present as hydroxide. In estimating the effect of the magnesia compounds in causing corrosion in boilers all the chlorine and the sulfuric acid in excess of that required to saturate the alkalies should be considered as combined with the magnesia. The table in the end of the book will be found useful in making these calculations.

The analysis should be reported in parts per million and in grains per gallon. To convert parts per million to grains per gallon multiply by 0.058353.

CHAPTER XXXIV

CALCULATION OF NORMAL SOLUTIONS

A normal solution, as used in this book, is a solution a liter of which contains 1 *gram atomic weight* of *active hydrogen or its equivalent.* Thus a normal solution of HCl will contain 1.008 grams of hydrogen or 36.468 grams of HCl in a liter, a liter of normal H_2SO_4 will contain 1.008 grams of hydrogen or 49.043 grams of H_2SO_4. A liter of normal NaOH contains 1.008 grams of hydrogen or 40.008 grams of NaOH, and a liter of normal NH_4OH contains 1.008 grams of *hydroxyl hydrogen* or 35.05 grams of NH_4OH. If an acid such as H_3PO_4 is used in a reaction wherein only two of its hydrogen atoms are active acid ions, a normal solution will contain one-half of the gram molecular weight of phosphoric acid in a liter, while if in the reaction all three of the hydrogen atoms are active a liter of normal phosphoric-acid solution will contain one-third of the gram atomic weight of phosphoric acid. That is, the amount of an acid or alkali contained in a liter of a normal solution depends upon the reaction for which the reagent is to be used, but it will always contain 1 gram atomic weight of hydrogen which will take part in the given reaction.

With oxidizing and reducing solutions the same principle holds good. For instance, 1 gram molecular weight of $KMnO_4$ in an acid solution will give up oxygen sufficient to oxidize 5.04 grams of hydrogen; therefore a normal solution of permanganate when it is to be used in an acid solution will contain one-fifth of the gram molecular weight of $KMnO_4$ per liter. In an alkaline solution 1 gram molecular weight of $KMnO_4$ will only oxidize the equivalent of 3.024 grams of hydrogen; therefore when it is to be used in an alkaline solution (as in the Volhard method for manganese) a liter of normal solution will contain one-third of the gram molecular weight of $KMnO_4$.

In making up normal solutions (or fractional normal solutions) of oxidizing or reducing reagents it is most convenient to consider

the change in valence which the reagent undergoes. Thus when permanganate is used to titrate iron as given on page 28, the manganese undergoes a change of valence from 7 to 2, that is, a normal permanganate solution contains one-fifth of its gram molecular weight in a liter. In the Volhard process the manganese undergoes a change of valence of 3 and a normal permanganate solution for use in the Volhard titration contains one-third of its gram molecular weight in a liter. Similarly when $K_2Cr_2O_7$ is used to titrate iron as directed on page 23, the chromium atoms undergo a change of valence of 3 each or 6 together. Therefore a normal solution of $K_2Cr_2O_7$ contains one-sixth of the gram molecular weight of $K_2Cr_2O_7$ in a liter.

When iron is titrated with an oxidizing agent it undergoes a change in valence of one. Therefore a liter of a normal solution of an oxidizing agent, as permanganate, will oxidize the gram atomic weight of iron or 55.84 grams and 1 c.c. will oxidize 0.05584 gram iron and 1 c.c. of a N/10 solution will oxidize (or titrate) 0.005584 gram of iron. The calculation for vanadium, manganese, chromium, etc., is done in the same way, remembering that the atomic weight of the element is divided by its change in valence.

When phosphorus is determined by the Emmerton process, the valence of the $(NH_4)_3PO_412MoO_3$ is reduced by 34; that is, a gram molecular weight of the "yellow precipitate" is reduced by the action of 34 grams of hydrogen, and when it is oxidized back by the standard permanganate enough permanganate must be used to oxidize the same amount of hydrogen or raise the valence of the reduced "yellow precipitate" molecule 34. Therefore a liter of a normal permanganate is equal to the gram atomic weight of phosphorus divided by 34 and 1 c.c. of a N/10 permanganate is equal to $31.04 \div 34 \times 10 \times 1000$ grams or 0.000091294 gram phosphorus.

The use of normal solutions (or fractional normal solutions) greatly simplifies calculations. One cubic centimeter of a normal acid will exactly neutralize 1 c.c. of a normal alkali, and 1 c.c. of a normal oxidizing solution will exactly oxidize 1 c.c. of a normal reducing solution (if they are capable of reacting with each other).

TABLE 1.—INTERNATIONAL ATOMIC WEIGHTS, 1916

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.88	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton (radium emanation)	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	3.99	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Yt	88.7
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

TABLE 2.—TABLE OF CHEMICAL FACTORS

(Calculated from 1913 Atomic Weights.)

Sought	Found	Factor	Sought	Found	Factor
Ag	AgCl	0.7526		$CdSO_4$	0.6159
	AgBr	0.5744	CdS	CdO	1.1252
	AgI	0.4595		$CdSO_4$	0.6930
Ag_2O	AgC	0.8084	Cl	AgCl	0.2474
Al	Al_2O_3	0.5303		Ag	0.3287
	$AlPO_4$	0.2219	HCl	AgCl	0.2544
Al_2O_3	$AlPO_4$	0.4184	HCl	Ag	0.3380
As	As_2S_3	0.6091	ClO_3	AgCl	0.5823
	As_2S_5	0.4832		KCl	1.1194
	$Mg_2As_2O_7$	0.4827		NaCl	1.4276
	$Mg_2P_2O_7$	0.6734	ClO_4	AgCl	0.6939
As_2O_3	As_2S_3	0.8041		KCl	1.3339
	As_2S_5	0.6378		NaCl	1.7013
	$Mg_2As_2O_7$	0.6372	CN	AgCN	0.1943
	$Mg_2P_2O_7$	0.8890		Ag	0.2411
AsO_3	As_2S_3	0.9992	HCNS	AgCNS	0.3560
	As_2S_5	0.7926		CuCNS	0.4857
	$Mg_2As_2O_7$	0.7919		$BaSO_4$	0.2531
As_2O_5	As_2S_3	0.9341	Co	$CoSO_4$	0.3804
	As_2S_5	0.7410	CoO	$CoSO_4$	0.4834
	$Mg_2As_2O_7$	0.7403	Cr	Cr_2O_3	0.6842
B	B_2O_3	0.3143		$PbCrO_4$	0.1609
BO_2	B_2O_3	1.2286		$BaCrO_4$	0.2052
BO_3	B_2O_3	1.6857		$K_2Cr_2O_7$	0.3535
B_4O_7	B_2O_3	1.1143	Cr_2O_3	$PbCrO_4$	0.2352
Ba	$BaSO_4$	0.5885		$BaCrO_4$	0.3000
	$BaCrO_4$	0.5422		$K_2Cr_2O_7$	0.5167
	$BaSiF_6$	0.4912	CrO_3	Cr_2O_3	1.3158
BaO	$BaSO_4$	0.6570		$PbCrO_4$	0.3095
	$BaCrO_4$	0.6053		$BaCrO_4$	0.3947
	$BaSiF_6$	0.5484	Cu	CuO	0.7989
Bi	Bi_2O_3	0.8965		Cu_2S	0.7986
	$BiAsO_4$	0.5994		CuCNS	0.5226
	BiOCl	0.8017		$CuSO_45H_2O$	0.2545
Bi_2O_3	Bi	1.1154	CuO	Cu_2S	0.9996
	BiOCl	1.1088		Cu	1.2517
Br	Ag	0.7408	F	CaF_2	0.4868
	AgBr	0.4256		$CaSO_4$	0.2792
	AgCl	0.5575	SiF_6	CaF_2	0.6074
C	CO_2	0.2727	Fe	Fe_2O_3	0.6994
CO_3	CO_2	1.3636		$(NH_4)_2Fe$	
Ca	CaO	0.7146		$(SO_4)_26H_2O$	0.1424
	$CaCO_3$	0.4004	FeO	Fe_2O_3	0.8998
	$CaSO_4$	0.2943	H	H_2O	0.1119
	CaF_2	0.5133	Hg	HgCl	0.8494
CaO	$CaCO_3$	0.5603		HgS	0.8618
	$CaSO_4$	0.4118	I	AgI	0.5406
	CaF_2	0.7182		AgCl	0.8855
$CaCO_3$	CaO	1.7847	K	KCl	0.5244
	$CaSO_4$	0.7350		K_2SO_4	0.4487
Cd	CdS	0.7780		$KClO_4$	0.2822
	CdO	0.8754		K_2PtCl_6	0.1609
	$CdSO_4$	0.5392	KCl	K_2SO_4	0.8557
CdO	CdS	0.8888		$KClO_4$	0.5381

TABLE 2.—TABLE OF CHEMICAL FACTORS—(*Continued*)

(Calculated from 1913 Atomic Weights.)

Sought	Found	Factor	Sought	Found	Factor
	K_2PtCl_6	0.3068		$P_2O_5 24MoO_3$	0.0172
K_2O	KCl	0.6317	P_2O_5	$Mg_2P_2O_7$	0.6379
	K_2SO_4	0.5405		$(NH_4)_3PO_4 12MoO_3$	0.0378
	$KClO_4$	0.3399	Pb	PbO	0.9283
	K_2PtCl_6	0.1938		PbS	0.8659
Li	Li_2SO_4	0.1262		PbO_2	0.8661
	LiCl	0.1637		$PbSO_4$	0.6831
Li_2O	Li_2SO_4	0.2718		$PbCrO_4$	0.6410
	LiCl	0.3524		$PbCl_2$	0.8025
Mg	MgO	0.6032	PbO	PbO_2	0.9331
	$MgSO_4$	0.2020		$PbSO_4$	0.7359
	$Mg_2P_2O_7$	0.2184		$PbCrO_4$	0.6905
MgO	$MgSO_4$	0.3349	S	$BaSO_4$	0.1374
	$Mg_2P_2O_7$	0.3622	SO_2	$BaSO_4$	0.2745
$MgCO_3$	$Mg_2P_2O_7$	0.7572	SO_3	$BaSO_4$	0.3430
Mn	$MnSO_4$	0.3638	SO_4	$BaSO_4$	0.4115
	MnS	0.6314	SO_4H_2	$BaSO_4$	0.4202
	Mn_3O_4	0.7203	H_2S	$BaSO_4$	0.1460
	$Mn_2P_2O_7$	0.3869	Sb	Sb_2O_4	0.7897
MnO	$MnSO_4$	0.4697		Sb_2S_3	0.7142
	MnS	0.8153	Sn	SnO_2	0.7881
	Mn_3O_4	0.9301	Si	SiO_2	0.4693
	$Mn_2P_2O_7$	0.4996	Sr	SrO	0.8456
Mo	MoO_3	0.6667		$SrCO_3$	0.5936
	$PbMoO_4$	0.2616		$SrSO_4$	0.4770
	Na_2O NaCl	0.5303		$Sr(NO_3)_2$	0.4140
N	NH_3	0.8225	SrO	$SrCO_3$	0.7019
	NH_4Cl	0.2619		$SrSO_4$	0.5641
	$(NH_4)_2PtCl_6$	0.0631		$Sr(NO_3)_2$	0.4896
NH_3	NH_4Cl	0.3182	Th	ThO_2	0.8790
	$(NH_4)_2PtCl_6$	0.0767	Ti	TiO_2	0.6005
Ni	NiO	0.7858	U	U_3O_8	0.8482
	$NiC_8H_{14}N_4O_4$	0.2032		UO_2	0.8817
NO_3H	NO	2.0999		$U_2P_2O_7$	0.7326
	NH_3	3.6995	V	V_2O_5	0.5614
	$(NH_4)_2PtCl_6$	0.2839	W	WO_3	0.7931
N_2O_5	NO	1.7997	Zn	ZnS	0.6709
	NH_3	3.1707		ZnO	0.8034
	$(NH_4)_2PtCl_6$	0.2433		$Zn_2P_2O_7$	0.4289
P	$Mg_2P_2O_7$	0.2787	Zr	ZrO_2	0.7390
	$(NH_4)_3PO_4$, $12MoO_3$	0.0165			

TABLE 3.—LOGARITHMS OF NUMBERS

N	0	1	2	3	4	5	6	7	8	9	d
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	41
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	38
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	35
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	32
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	30
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	28
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	26
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	25
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	24
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	22
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	21
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	20
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	19
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	18
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	18
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	17
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	16
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	16
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	15
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	15
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	14
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	14
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	13
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	13
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	13
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	12
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	12
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	12
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	11
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	11
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	11
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	10
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	10
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	10
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	10
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	10
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	9
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	9
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	9
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	9
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	8
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	8
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	8
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	8
N	0	1	2	3	4	5	6	7	8	9	d

TABLE 3.—LOGARITHMS OF NUMBERS—(*Continued*)

N	0	1	2	3	4	5	6	7	8	9	d
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	8
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	8
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	8
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	7
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	7
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	7
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	7
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	7
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	7
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	7
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	6
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	6
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	6
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	6
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	6
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	6
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	5
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	5
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	5
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	5
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	5
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	5
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	5
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	5
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	5
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	4
100	0000	0004	0009	0013	0017	0022	0026	0030	0035	0039	4
N	0	1	2	3	4	5	6	7	8	9	d

TABLE 4.—SPECIFIC GRAVITY OF HCl, HNO_3, AND H_2SO_4 AT 15° IN VACUO[1]

Sp. Gr.	Per cent. by weight			Sp. Gr.	Per cent. by weight
	HCl	HNO_3	H_2SO_4		H_2SO_4
1.000	0.16	0.10	0.09	1.570	66.09
1.010	2.14	1.90	1.57	1.580	66.95
1.020	4.13	3.70	3.03	1.590	67.83
1.030	6.15	5.50	4.49	1.600	68.70
1.040	8.16	7.26	5.96	1.610	69.56
1.050	10.17	8.99	7.37	1.620	70.42
1.060	12.19	10.67	8.77	1.630	71.27
1.070	14.17	12.32	10.19	1.640	72.12
1.080	16.15	13.94	11.60	1.650	72.96
1.090	18.11	15.52	12.99	1.660	73.81
1.100	20.01	17.10	14.35	1.670	74.66
1.110	21.92	18.66	15.71	1.680	75.50
1.120	23.82	20.22	17.01	1.690	76.38
1.130	25.75	21.76	18.31	1.700	77.17
1.140	27.66	23.30	19.61	1.710	78.04
1.150	29.57	24.83	20.91	1.720	78.92
1.160	31.52	26.35	22.19	1.730	79.80
1.170	33.46	27.87	23.47	1.740	80.68
1.180	35.39	29.37	24.76	1.750	81.56
1.190	37.23	30.87	26.04	1.760	82.44
1.200	39.11	32.34	27.32	1.770	83.51
1.210		33.80	28.58	1.780	84.50
1.220		35.26	29.84	1.790	85.70
1.230		36.76	31.11	1.800	86.92
1.240		38.27	32.28	1.810	88.30
1.250		39.80	33.43	1.820	90.05
1.260		41.32	34.57	1.830	92.10
1.270		42.85	35.71	1.840	95.70
1.280		44.39	36.87	1.841	96.38
1.290		45.93	38.03	1.8415	97.35
1.300		47.47	39.19	1.841	98.20
1.310		49.05	40.35	1.840	98.72
1.320		50.69	41.50	1.839	99.12
1.330		52.34	42.66		
1.340		54.04	43.74		
1.350		55.76	44.82		
1.360		57.54	45.88		
1.370		59.36	46.94		
1.380		61.24	48.00		
1.390		63.20	49.06		
1.400		65.27	50.11		
1.410		67.47	51.15		
1.420		69.77	52.15		
1.430		72.14	53.11		
1.440		74.64	54.07		
1.450		77.24	55.03		
1.460		79.94	55.97		
1.470		82.86	56.90		
1.480		86.01	57.83		
1.490		89.86	58.74		
1.500		94.04	59.70		
1.510		98.05	60.65		
1.520		99.62	61.59		
1.530			62.53		
1.540			63.43		
1.550			64.26		
1.560			65.20		

[1] LUNGE-BERL. Chem. tech. Untersungsmethoden, 6th edition, Vol. 1.

TABLE 5.—SPECIFIC GRAVITY OF KOH, NaOH, AND NH_3 SOLUTIONS AT 15° C.

Sp. Gr.	Per cent. KOH	Per cent. NaOH	Sp. Gr.	Per cent. NH_3
1.007	0.9	0.59	1.000	0.00
1.022	2.6	1.65	0.996	0.91
1.037	4.5	3.22	0.992	1.84
1.052	6.4	4.50	0.988	2.80
1.067	8.2	5.86	0.984	3.80
1.083	10.1	7.30	0.980	4.80
1.100	12.0	8.78	0.976	5.80
1.116	13.8	10.30	0.972	6.80
1.134	15.7	11.90	0.968	7.82
1.152	17.6	13.50	0.964	8.84
1.171	19.5	15.15	0.960	9.91
1.190	21.4	16.91	0.956	11.03
1.210	23.3	18.71	0.952	12.17
1.231	25.1	20.69	0.948	13.31
1.252	27.0	22.50	0.944	14.46
1.274	28.9	24.48	0.940	15.63
1.297	30.7	26.58	0.936	16.82
1.320	32.7	28.83	0.932	18.03
1.345	34.9	31.20	0.928	19.25
1.370	36.9	33.73	0.924	20.49
1.397	38.9	36.36	0.920	21.75
1.424	40.9	39.06	0.916	23.03
1.453	43.4	42.02	0.912	24.33
1.483	45.8	45.16	0.908	25.65
1.514	48.3	48.41	0.904	26.98
1.546	50.6	.....	0.900	28.33
1.580	53.2	.....	0.896	29.69
1.615	55.9	.....	0.892	31.05
1.634	57.5	.....	0.888	32.50
		.....	0.884	34.10

TABLE 6.—SPECIFIC GRAVITY OF ACETIC ACID AT 15° C.

Specific gravity	Per cent. $H.C_2H_3O_2$	Specific gravity	Per cent. $H.C_2H_3O_2$	Specific gravity	Per cent. $H.C_2H_3O_2$	Specific gravity	Per cent. $H.C_2H_3O_2$
0.9992	0	1.0363	26	1.0623	51	1.0747	76
1.0007	1	1.0375	27	1.0631	52	1.0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1.0412	30	1.0653	55	1.0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1.0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1.0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1.0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1.0523	40	1.0712	65	1.0713	90
1.0214	15	1.0533	41	1.0717	66	1.0705	91
1.0228	16	1.0543	42	1.0721	67	1.0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1.0553	100
1.0350	25						

TABLE 7.—SPECIFIC GRAVITY AND PERCENTAGE OF ALCOHOL BY VOLUME
(Squib)

Per cent. alcohol by volume	Specific gravity at 15.56°C./15.56°	Per cent. alcohol by volume	Specific gravity at 15.56°C./15.56°	Per cent. alcohol by volume	Specific gravity at 15.56°C./15.56°	Per cent. alcohol by volume	Specific gravity at 15.56°C./15.56°
1	0.9985	26	0.9698	51	0.9323	76	0.8745
2	0.9970	27	0.9691	52	0.9303	77	0.8721
3	0.9956	28	0.9678	53	0.9283	78	0.8696
4	0.9942	29	0.9665	54	0.9262	79	0.8664
5	0.9930	30	0.9652	55	0.9242	80	0.8639
6	0.9914	31	0.9643	56	0.9221	81	0.8611
7	0.9898	32	0.9631	57	0.9200	82	0.8581
8	0.9890	33	0.9618	58	0.9178	83	0.8557
9	0.9878	34	0.9609	59	0.9160	84	0.8526
10	0.9869	35	0.9593	60	0.9135	85	0.8496
11	0.9855	36	0.9578	61	0.9113	86	0.8466
12	0.9841	37	0.9565	62	0.9090	87	0.8434
13	0.9828	38	0.9550	63	0.9069	88	0.8408
14	0.9821	39	0.9535	64	0.9047	89	0.8373
15	0.9815	40	0.9519	65	0.9025	90	0.8340
16	0.9802	41	0.9503	66	0.9001	91	0.8305
17	0.9789	42	0.9490	67	0.8973	92	0.8272
18	0.9778	43	0.9470	68	0.8949	93	0.8237
19	0.9766	44	0.9452	69	0.8925	94	0.8199
20	0.9760	45	0.9434	70	0.8900	95	0.8164
21	0.9753	46	0.9416	71	0.8875	96	0.8125
22	0.9741	47	0.9396	72	0.8850	97	0.8084
23	0.9728	48	0.9381	73	0.8825	98	0.8041
24	0.9716	49	0.9362	74	0.8799	99	0.7995
25	0.9709	50	0.9343	75	0.8769	100	0.7946

TABLE 8.—REDUCTION OF THE VOLUME OF N/10 SOLUTIONS TO THE VOLUME AT 20° C. (CORRECTIONS GIVEN IN 1/100 CUBIC CENTIMETERS)

Burette reading	6°	8°	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30°
5 cc.	0	0	0	0	0	0	0	0	0	−0	−1	−1	−1
10 cc.	+1	+1	+1	+1	+1	0	0	0	0	−1	−1	−2	−2
15 cc.	+2	+2	+2	+2	+1	+1	0	0	0	−1	−2	−2	−3
20 cc.	+3	+3	+3	+2	+2	+1	0	0	−1	−2	−2	−3	−4
25 cc.	+4	+3	+3	+3	+2	+2	+1	0	−1	−2	−3	−4	−5
30 cc.	+4	+4	+4	+3	+3	+2	+1	0	−1	−2	−4	−5	−6
35 cc.	+5	+5	+4	+4	+3	+2	+1	0	−1	−3	−4	−6	−7
40 cc.	+6	+6	+5	+5	+3	+2	+2	0	−2	−3	−5	−6	−8
45 cc.	+6	+6	+5	+5	+4	+3	+2	0	−2	−4	−5	−7	−9
50 cc.	+7	+7	+6	+6	+4	+3	+2	0	−2	−4	−6	−8	−10

TABLE 9.—DENSITY OF WATER AT 0° TO 36°

WEIGHT IN GRAMS OF 1 CUBIC CENTIMETER OF WATER FREE FROM AIR AT TEMPERATURES OF 0 TO 36 CENTIGRADE BY THE HYDROGEN THERMOMETER—ACCORDING TO THIESEN, SCHEEL, AND DIESSELHORST WISS. ABH. D. PHYS.—TECHN. REICHSANAT. 3, 68, 1900

Degrees	Tenths of Degrees									
	0	.1	.2	.3	.4	.5	.6	.7	.8	.9
0	0.999868	874	881	887	893	899	905	911	916	922
1	927	932	936	941	945	950	954	957	961	965
2	968	971	974	977	980	982	985	987	989	991
3	992	994	995	996	997	998	999	999	*000	*000
4	1.000000	000	000	*999	*999	*998	*997	*996	*995	*993
5	0.999992	990	988	986	984	982	979	977	974	971
6	986	965	962	958	954	951	947	943	938	934
7	929	925	920	915	910	904	899	893	888	882
8	876	870	864	857	851	844	837	830	823	816
9	808	801	793	785	778	769	761	753	744	736
10	727	718	709	700	691	681	672	662	652	642
11	632	622	612	601	591	580	569	558	547	536
12	525	513	502	490	478	466	454	442	429	417
13	404	391	379	366	353	339	326	312	299	285
14	271	257	243	229	215	200	186	171	156	141
15	126	111	096	081	065	050	034	018	002	*986
16	0.998970	953	937	920	904	887	870	853	836	819
17	801	784	766	749	731	713	695	677	659	640
18	622	603	585	566	547	528	509	490	471	451
19	432	412	392	372	352	332	312	292	271	251
20	230	210	189	168	147	126	105	083	062	040
21	019	*997	*975	*953	*931	*909	*887	*864	*842	*819
22	0.997797	774	751	728	705	682	659	635	612	588
23	565	541	517	493	469	445	421	396	372	347
24	323	298	273	248	223	198	173	147	122	096
25	071	045	019	*994	*968	*941	*915	*889	*863	*836
26	0.996810	783	756	730	703	676	648	621	594	567
27	539	512	484	456	428	400	372	344	316	288
28	259	231	202	174	145	116	087	058	029	000
29	0.995971	941	912	882	853	823	793	763	733	703
30	673	643	613	582	552	521	491	460	429	398
31	367	336	305	273	242	211	179	148	116	084
32	052	020	*988	*956	*924	*892	*859	*827	*794	*762
33	0.994729	696	663	630	597	564	531	498	464	431
34	398	364	330	296	263	229	195	161	126	092
35	058	023	*989	*954	*920	*885	*850	*815	*780	*745

TABLE 10.—HEAT OF COMBUSTION OF FUEL GAS CONSTITUENTS IN SMALL CALORIES PER GRAM-MOLECULE (VALUE AT CONSTANT PRESSURE), BASED ON LANDOLT AND BORNSTEIN'S TABLES

Constituent	Heat of combustion	Products of combustion
Carbon (C) (solid)	97,000	CO_2
Carbon monoxide (CO)	68,000	CO_2
Hydrogen (H_2)	58,330	H_2O (gas)
Hydrogen (H_2)	69,000	H_2O (liquid)
Methane (CH_4)	192,160	CO_2 and H_2O (gas)
Methane (CH_4)	213,500	CO_2 and H_2O (liquid)
Ethane (C_2H_6)	340,300	CO_2 and H_2O (gas)
Ethane (C_2H_6)	372,300	CO_2 and H_2O (liquid)
Ethylene (C_2H_4)	319,760	CO_2 and H_2O (gas)
Ethylene (C_2H_4)	341,100	CO_2 and H_2O (liquid)
Acetylene (C_2H_2)	301,630	CO_2 and H_2O (gas)
Acetylene (C_2H_2)	312,300	CO_2 and H_2O (liquid)
Benzene (C_6H_6) (gas)	757,000	CO_2 and H_2O (gas)
Benzene (C_6H_6) (gas)	789,000	CO_2 and H_2O (liquid)
Benzene (C_6H_6) (liquid)	749,200	CO_2 and H_2O (gas)
Benzene (C_6H_6) (liquid)	781,200	CO_2 and H_2O (liquid)
Methyl alcohol (CH_3OH) (gas)	158,660	CO_2 and H_2O (gas)
Methyl alcohol (CH_3OH) (gas)	180,000	CO_2 and H_2O (liquid)
Methyl alcohol (CH_3OH) (liquid)	149,360	CO_2 and H_2O (gas)
Methyl alcohol (CH_3OH) (liquid)	170,700	CO_2 and H_2O (liquid)
Ethyl alcohol (C_2H_5OH) (gas)	305,400	CO_2 and H_2O (gas)
Ethyl alcohol (C_2H_5OH) (gas)	337,400	CO_2 and H_2O (liquid)
Ethyl alcohol (C_2H_5OH) (liquid)	294,700	CO_2 and H_2O (gas)
Ethyl alcohol (C_2H_5OH) (liquid)	326,700	CO_2 and H_2O (liquid)

TABLE 11.—TENSION OF WATER VAPOR ACCORDING TO REGNAULT

Degrees C.	Tension in millimeters	Degrees C.	Tension in millimeters	Degrees C.	Tension in millimeters
1	4.940	13	11.162	25	23.550
2	5.302	14	11.908	26	24.988
3	5.687	15	12.699	27	26.505
4	6.097	16	13.536	28	28.101
5	6.534	17	14.421	29	29.782
6	6.998	18	15.357	30	31.548
7	7.492	19	16.346	31	33.405
8	8.017	20	17.391	32	35.359
9	8.574	21	18.495	33	37.410
10	9.165	22	19.659	34	39.565
11	9.792	23	20.888	35	41.827
12	10.457	24	22.184		

TABLE 12.—VOLUME OF GAS AT 0° C. AND 760 MM. EQUIVALENT TO 1 LITER AT OBSERVED TEMPERATURE AND PRESSURE

Based upon absolute zero = −273.000° C. Ohio State University School of Mines

Temp., °C	700	702	704	706	708	710	712	714	716	718	720
0°	.9211	.9237	.9263	.9290	.9316	.9342	.9368	.9395	.9421	.9447	.9474
2°	.9144	.9170	.9186	.9222	.9248	.9274	.9300	.9326	.9353	.9379	.9405
4°	.9078	.9103	.9129	.9155	.9181	.9207	.9233	.9259	.9285	.9311	.9337
6°	.9013	.9038	.9064	.9090	.9116	.9141	.9167	.9193	.9219	.9244	.9270
8°	.8948	.8974	.8999	.9025	.9051	.9076	.9102	.9127	.9153	.9179	.9204
10°	.8885	.8911	.8936	.8961	.8987	.9012	.9038	.9063	.9088	.9114	.9139
12°	.8823	.8848	.8873	.8898	.8924	.8949	.8974	.8999	.9024	.9050	.9075
14°	.8761	.8786	.8811	.8836	.8861	.8886	.8911	.8936	.8962	.8987	.9012
16°	.8701	.8725	.8750	.8775	.8800	.8825	.8850	.8875	.8899	.8924	.8949
18°	.8641	.8666	.8691	.8715	.8740	.8764	.8789	.8814	.8838	.8863	.8888
20°	.8582	.8606	.8631	.8655	.8680	.8704	.8729	.8753	.8778	.8802	.8827
22°	.8524	.8548	.8572	.8597	.8621	.8645	.8670	.8694	.8718	.8743	.8767
24°	.8466	.8491	.8515	.8539	.8563	.8587	.8611	.8636	.8660	.8684	.8708
26°	.8410	.8434	.8458	.8482	.8506	.8530	.8554	.8578	.8602	.8626	.8650
28°	.8354	.8378	.8402	.8425	.8449	.8473	.8497	.8521	.8545	.8569	.8593
30°	.8299	.8322	.8346	.8370	.8393	.8417	.8441	.8465	.8488	.8512	.8536
32°	.8244	.8268	.8291	.8315	.8338	.8362	.8386	.8409	.8433	.8456	.8480
34°	.8191	.8214	.8237	.8261	.8284	.8308	.8331	.8354	.8378	.8401	.8425
36°	.8138	.8161	.8184	.8207	.8231	.8254	.8277	.8300	.8324	.8347	.8370
38°	.8085	.8108	.8131	.8154	.8177	.8201	.8224	.8247	.8270	.8293	.8316
40°	.8034	.8056	.8079	.8102	.8125	.8148	.8171	.8194	.8217	.8240	.8263

TABLE 12.—VOLUME OF GAS AT 0°C. AND 760 MM. EQUIVALENT TO 1 LITER AT OBSERVED TEMPERATURE AND PRESSURE—(*Continued*)

Temp., °C.	722	724	726	728	730	732	734	736	738	740
0°	.9500	.9526	.9553	.9579	.9605	.9632	.9658	.9684	.9711	.9737
2°	.9431	.9457	.9483	.9509	.9535	.9562	.9588	.9614	.9640	.9666
4°	.9363	.9389	.9415	.9441	.9467	.9492	.9518	.9544	.9570	.9596
6°	.9296	.9322	.9347	.9373	.9399	.9425	.9450	.9476	.9502	.9528
8°	.9230	.9255	.9281	.9306	.9332	.9357	.9383	.9409	.9434	.9460
10°	.9164	.9190	.9215	.9241	.9266	.9291	.9317	.9342	.9368	.9393
12°	.9100	.9125	.9150	.9176	.9201	.9226	.9251	.9277	.9302	.9327
14°	.9037	.9062	.9087	.9112	.9137	.9162	.9187	.9212	.9237	.9262
16°	.8974	.8999	.9024	.9049	.9074	.9098	.9123	.9148	.9173	.9198
18°	.8912	.8937	.8962	.8987	.9011	.9036	.9061	.9085	.9110	.9135
20°	.8852	.8876	.8901	.8925	.8950	.8974	.8999	.9023	.9048	.9072
22°	.8791	.8816	.8840	.8865	.8889	.8913	.8938	.8962	.8986	.9011
24°	.8732	.8757	.8781	.8805	.8829	.8853	.8878	.8902	.8926	.8950
26°	.8674	.8698	.8722	.8746	.8770	.8794	.8818	.8842	.8866	.8890
28°	.8616	.8640	.8664	.8688	.8712	.8736	.8760	.8783	.8807	.8831
30°	.8559	.8583	.8607	.8631	.8654	.8678	.8702	.8725	.8749	.8773
32°	.8503	.8527	.8550	.8574	.8598	.8621	.8645	.8668	.8692	.8715
34°	.8448	.8471	.8495	.8518	.8542	.8565	.8588	.8612	.8635	.8659
36	.8393	.8417	.8440	.8463	.8486	.8510	.8533	.8556	.8579	.8603
38°	.8339	.8362	.8385	.8409	.8432	.8455	.8478	.8501	.8524	.8547
40°	.8286	.8309	.8332	.8355	.8378	.8401	.8424	.8447	.8470	.8493

TABLE 12.—VOLUME OF GAS AT 0°C. AND 760 MM. EQUIVALENT TO 1 LITER AT OBSERVED TEMPERATURE AND PRESSURE—(*Continued*)

Temp., °C.	742	744	746	748	750	752	754	756	758	760
0°	.9763	.9790	.9816	.9842	.9868	.9895	.9921	.9947	.9974	1.0000
2°	.9692	.9718	.9744	.9771	.9797	.9823	.9849	.9875	.9901	.9927
4°	.9622	.9648	.9674	.9700	.9726	.9752	.9778	.9804	.9830	.9856
6°	.9553	.9579	.9605	.9631	.9656	.9682	.9708	.9734	.9759	.9785
8°	.9485	.9511	.9536	.9562	.9588	.9613	.9639	.9664	.9690	.9715
10°	.9418	.9444	.9469	.9494	.9520	.9545	.9571	.9596	.9621	.9647
12°	.9352	.9377	.9403	.9428	.9453	.9478	.9503	.9529	.9554	.9579
14°	.9287	.9312	.9337	.9362	.9387	.9412	.9437	.9462	.9487	.9512
16°	.9223	.9248	.9272	.9297	.9322	.9347	.9372	.9397	.9422	.9446
18°	.9159	.9184	.9209	.9233	.9258	.9283	.9307	.9332	.9357	.9381
20°	.9097	.9121	.9146	.9170	.9195	.9219	.9244	.9268	.9293	.9317
22°	.9035	.9059	.9084	.9108	.9132	.9157	.9181	.9205	.9230	.9254
24°	.8974	.8998	.9023	.9047	.9071	.9095	.9119	.9144	.9168	.9192
26°	.8914	.8938	.8962	.8986	.9010	.9034	.9058	.9082	.9106	.9130
28°	.8855	.8879	.8903	.8927	.8951	.8974	.8998	.9022	.9046	.9070
30°	.8797	.8820	.8844	.8868	.8891	.8915	.8939	.8963	.8986	.9010
32°	.8739	.8762	.8786	.8810	.8833	.8857	.8880	.8904	.8927	.8951
34°	.8682	.8705	.8729	.8752	.8776	.8799	.8822	.8846	.8869	.8893
36°	.8626	.8649	.8672	.8696	.8719	.8742	.8765	.8789	.8812	.8835
38°	.8570	.8593	.8616	.8640	.8663	.8686	.8709	.8732	.8755	.8778
40°	.8516	.8538	.8561	.8584	.8607	.8630	.8653	.8676	.8699	.8722

TABLE 13.—VOLUME OF GAS AT OBSERVED TEMPERATURE AND PRESSURE EQUIVALENT TO 1 LITER AT 0° C. AND 760 MM. MERCURY

Based Upon Absolute Zero = −273.000° C. Ohio State University—School of Mines

Temp., °C.	700	702	704	706	708	710	712	714	716	718	720
0°	1.0857	1.0826	1.0795	1.0765	1.0735	1.0705	1.0674	1.0645	1.0615	1.0585	1.0556
2°	1.0937	1.0906	1.0875	1.0844	1.0813	1.0783	1.0752	1.0722	1.0692	1.0663	1.0633
4°	1.1016	1.0985	1.0954	1.0923	1.0892	1.0861	1.0831	1.0800	1.0770	1.0740	1.0710
6°	1.1096	1.1064	1.1032	1.1001	1.0970	1.0940	1.0909	1.0878	1.0848	1.0818	1.0787
8°	1.1175	1.1144	1.1112	1.1080	1.1049	1.1018	1.0987	1.0956	1.0925	1.0895	1.0865
10°	1.1255	1.1223	1.1191	1.1159	1.1128	1.1096	1.1065	1.1034	1.1003	1.0973	1.0942
12°	1.1334	1.1302	1.1270	1.1238	1.1206	1.1175	1.1144	1.1112	1.1081	1.1050	1.1020
14°	1.1414	1.1382	1.1349	1.1317	1.1285	1.1253	1.1222	1.1190	1.1159	1.1128	1.1097
16°	1.1493	1.1461	1.1428	1.1396	1.1364	1.1332	1.1300	1.1268	1.1237	1.1206	1.1174
18°	1.1573	1.1540	1.1507	1.1475	1.1442	1.1410	1.1378	1.1346	1.1314	1.1283	1.1252
20°	1.1653	1.1620	1.1587	1.1554	1.1521	1.1489	1.1456	1.1424	1.1392	1.1361	1.1329
22°	1.1732	1.1699	1.1665	1.1632	1.1600	1.1567	1.1535	1.1502	1.1470	1.1438	1.1406
24°	1.1812	1.1778	1.1744	1.1711	1.1678	1.1645	1.1612	1.1580	1.1548	1.1516	1.1484
26°	1.1891	1.1858	1.1824	1.1790	1.1757	1.1724	1.1691	1.1658	1.1625	1.1593	1.1561
28°	1.1971	1.1937	1.1903	1.1869	1.1835	1.1802	1.1769	1.1736	1.1703	1.1671	1.1638
30°	1.2050	1.2016	1.1982	1.1948	1.1914	1.1881	1.1847	1.1814	1.1781	1.1748	1.1716
32°	1.2130	1.2095	1.2061	1.2027	1.1993	1.1959	1.1925	1.1892	1.1859	1.1826	1.1793
34°	1.2209	1.2175	1.2140	1.2106	1.2072	1.2038	1.2004	1.1970	1.1937	1.1903	1.1870
36°	1.2288	1.2254	1.2219	1.2185	1.2150	1.2116	1.2082	1.2048	1.2014	1.1981	1.1948
38°	1.2368	1.2333	1.2298	1.2263	1.2229	1.2194	1.2160	1.2126	1.2092	1.2058	1.2025
40°	1.2448	1.2413	1.2377	1.2342	1.2307	1.2273	1.2238	1.2204	1.2170	1.2136	1.2102

TABLE 13.— VOLUME OF GAS AT OBSERVED TEMPERATURE AND PRESSURE EQUIVALENT TO 1 LITER AT 0° C. AND 760 MM. MERCURY—(*Continued*)

Temp., °C.	722	724	726	728	730	732	734	736	738	740
0°	1.0527	1.0497	1.0469	1.0440	1.0411	1.0383	1.0354	1.0326	1.0298	1.0270
2°	1.0604	1.0574	1.0545	1.0516	1.0487	1.0459	1.0430	1.0401	1.0373	1.0345
4°	1.0681	1.0651	1.0622	1.0593	1.0564	1.0535	1.0506	1.0478	1.0449	1.0421
6°	1.0758	1.0728	1.0698	1.0669	1.0640	1.0611	1.0582	1.0553	1.0524	1.0496
8°	1.0835	1.0805	1.0775	1.0745	1.0716	1.0687	1.0658	1.0629	1.0600	1.0571
10°	1.0912	1.0882	1.0852	1.0822	1.0792	1.0763	1.0733	1.0704	1.0675	1.0646
12°	1.0989	1.0959	1.0929	1.0899	1.0869	1.0839	1.0809	1.0780	1.0751	1.0722
14°	1.1066	1.1036	1.1005	1.0975	1.0945	1.0915	1.0885	1.0856	1.0826	1.0797
16°	1.1143	1.1113	1.1108	1.1051	1.1021	1.0991	1.0961	1.0932	1.0902	1.0872
18°	1.1220	1.1189	1.1159	1.1128	1.1097	1.1067	1.1037	1.1007	1.0977	1.0948
20°	1.1298	1.1267	1.1235	1.1204	1.1174	1.1143	1.1113	1.1083	1.1053	1.1023
22°	1.1375	1.1343	1.1312	1.1281	1.1250	1.1219	1.1189	1.1158	1.1128	1.1098
24°	1.1452	1.1420	1.1389	1.1357	1.1326	1.1295	1.1264	1.1234	1.1203	1.1173
26°	1.1529	1.1497	1.1465	1.1434	1.1403	1.1371	1.1340	1.1310	1.1279	1.1248
28°	1.1606	1.1574	1.1542	1.1510	1.1479	1.1447	1.1416	1.1385	1.1354	1.1324
30°	1.1683	1.1651	1.1619	1.1587	1.1555	1.1523	1.1492	1.1461	1.1430	1.1399
32°	1.1760	1.1728	1.1696	1.1663	1.1631	1.1600	1.1568	1.1537	1.1505	1.1474
34°	1.1837	1.1805	1.1772	1.1740	1.1708	1.1676	1.1644	1.1612	1.1581	1.1549
36°	1.1915	1.1882	1.1849	1.1816	1.1784	1.1752	1.1720	1.1688	1.1656	1.1625
38°	1.1992	1.1959	1.1925	1.1893	1.1860	1.1828	1.1795	1.1763	1.1732	1.1700
40°	1.2069	1.2035	1.2002	1.1969	1.1936	1.1903	1.1871	1.1839	1.1807	1.1775

TABLE 13.—VOLUME OF GAS AT OBSERVED TEMPERATURE AND PRESSURE EQUIVALENT TO 1 LITER AT 0° C. AND 760 MM. MERCURY—(*Continued*)

Temp., °C.	742	744	746	748	750	752	754	756	758	760
0°	1.0243	1.0215	1.0188	1.0160	1.0133	1.0107	1.0080	1.0053	1.0026	1.0000
2°	1.0318	1.0290	1.0262	1.0235	1.0207	1.0180	1.0153	1.0127	1.0100	1.0073
4°	1.0393	1.0365	1.0337	1.0310	1.0282	1.0255	1.0227	1.0200	1.0173	1.0147
6°	1.0468	1.0439	1.0411	1.0384	1.0356	1.0329	1.0301	1.0274	1.0247	1.0220
8°	1.0543	1.0514	1.0486	1.0458	1.0430	1.0403	1.0375	1.0348	1.0320	1.0293
10°	1.0618	1.0589	1.0561	1.0533	1.0505	1.0477	1.0449	1.0421	1.0393	1.0366
12°	1.0693	1.0664	1.0635	1.0607	1.0579	1.0551	1.0523	1.0495	1.0467	1.0440
14°	1.0768	1.0739	1.0710	1.0681	1.0653	1.0625	1.0597	1.0568	1.0540	1.0513
16°	1.0843	1.0814	1.0785	1.0756	1.0728	1.0699	1.0670	1.0642	1.0614	1.0586
18°	1.0918	1.0889	1.0859	1.0830	1.0801	1.0773	1.0744	1.0716	1.0687	1.0659
20°	1.0993	1.0964	1.0934	1.0905	1.0876	1.0847	1.0818	1.0790	1.0762	1.0733
22°	1.1068	1.1038	1.1009	1.0979	1.0950	1.0921	1.0892	1.0863	1.0834	1.0806
24°	1.1143	1.1113	1.1083	1.1054	1.1024	1.0995	1.0966	1.0937	1.0908	1.0879
26°	1.1218	1.1188	1.1158	1.1128	1.1098	1.1069	1.1040	1.1010	1.0981	1.0952
28°	1.1293	1.1263	1.1232	1.1202	1.1173	1.1143	1.1113	1.1084	1.1055	1.1026
30°	1.1368	1.1338	1.1307	1.1277	1.1247	1.1217	1.1187	1.1158	1.1129	1.1099
32°	1.1443	1.1412	1.1382	1.1351	1.1321	1.1291	1.1261	1.1231	1.1201	1.1172
34°	1.1518	1.1487	1.1456	1.1426	1.1395	1.1365	1.1335	1.1305	1.1275	1.1245
36°	1.1593	1.1562	1.1531	1.1500	1.1470	1.1440	1.1410	1.1379	1.1349	1.1319
38°	1.1668	1.1637	1.1606	1.1575	1.1544	1.1513	1.1483	1.1452	1.1422	1.1392
40°	1.1743	1.1711	1.1680	1.1649	1.1618	1.1587	1.1556	1.1526	1.1495	1.1465

TABLE 14.—USE OF THE COMMON INDICATORS

Substance titrated	Methyl orange	Phenolphthalein	Other indicators
Acetic acid	Useless	Good.	
Citric acid	Useless	Good.	
Oxalic acid	Useless	Good	Litmus is good.
Phosphoric acid	Good. Changes at NaH_2PO_4.	End at Na_2HPO_4, but indistinct.	Cochineal is good with change at Na_2HPO_4.
HCl, HNO_3, H_2SO_4	Good	Good.	
Ammonia	Good	Useless	Cochineal and methyl red are good.
Na_2CO_3, K_2CO_3	Good. Changes at 2NaCl and 2KCl.	End at $NaHCO_3$, but not sharp.	Cochineal is good.
Bicarbonates	Good	Useless	Cochineal is good.
Sulfurous acid	Good. Changes at $NaHSO_3$.		
NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$.	Good	Good.	
Borates	Good. Not affected by H_3BO_3.	Useless	Lacmoid is good.
Alkali metal silicates		Good. Not affected by H_4SiO_4.	
Cyanides	Good.		
Amines	Good		Methyl red is good.
Pyridine	Useless		Methyl red is good.
MoO_3, WO_3	Good. Changes at Na_2MoO_4, etc.		
	Is in general a good indicator for strong acids and strong bases and weak bases, but is useless for weak acids. Color is red in acid and yellow in alkalies. Must be used cold.	Is in general a good indicator for strong acids and strong bases and weak acids, but is useless for weak bases. CO_2 must be absent at the end. Color is red in alkaline and colorless in acid solutions.	

Standard solutions used for titrating are assumed to be HCl and NaOH.

TABLE 15.—MEASURES AND WEIGHTS

Measures of Capacity

A. Dry Measure

1 bushel = 2150.42 cubic inches.
1 bushel = the volume of 77.627 pounds of distilled water at 4° C.
Legal: 1 liter = 0.908 quart.
1 bushel = 4 pecks = 8 gallons = 32 quarts = 35.24229 liters.
1 peck = 2 gallons = 8 quarts = 8.81057 liters.
1 gallon = 4 quarts = 4.40528 liters.
1 quart = 1.10132 liters.

B. Liquid Measure

1 U. S. gallon = 231 cubic inches.
1 gallon = the volume of 8.3388822 pounds = 58378 troy grains of distilled water at 4° C. (Stillman, Engineering Chemistry.)
1 gallon = 58318 grains of water at 62° F. (U. S. Phar.)
1 gallon = 58334.9+ grains of pure water at 60° F., weighed in air at 60° F., at barometric pressure of 30 inches of mercury. (Mason, Examination of Water.)
Legal: 1 liter = 1.0567 quart = 0.26417 gallon.
1 gallon = 4 quarts = 8 pints = 32 gills = 3.78544 liters.
1 quart = 2 pints = 8 gills = 0.94636 liter.
1 pint = 4 gills = 0.47318 liter.
1 gill = 0.118295 liter.
1 cubic foot = 7.48 gallons = 28.315 liters = 62.42 pounds of water at 60° F. (Stillman.)
1 cubic foot of water at 62° F. = 62.355 pounds avoirdupois = 28320 grams.
1 cubic inch of water at 62° F. = 0.0361 pounds avoirdupois = 16.387 grams. (Watts' Dictionary, V, 1010.)

Linear Measure

1 yard = 0.91440 meter.
1 foot = 0.30480 meter.
1 inch = 0.0254 meter.
39.37 inches = 1 meter.

Weights

1 grain troy = 0.0648004 gram.
1 pound troy = 0.822857 pounds avoirdupois.
1 pound avoirdupois = 7000 grains troy = 1.215279 pounds troy.

Troy Weight

1 pound = 12 oz. = 240 pwts. = 5760 grains = 373.2418 grams.
1 oz. = 20 pwts. = 480 grains = 31.1035 grams.
1 pwt. = 24 grains = 1.5552 grams.
1 grain = 0.0648 grams.
1 gram = 15.432 troy grains.

Avoirdupois Weight

1 ton = 20 hundredweight = 2240 pounds = 1016.04 kilograms.
1 hundredweight = 112 pounds = 50.80 kilograms.
1 pound = 16 ounces = 256 drams = 7000.00 grains = 453.5900 grams.
1 ounce = 16 drams = 437.50 grains = 28.3495 grams.
1 dram = 27.34 grains = 1.7718 grams.
1 net ton = 2000 pounds = 29166⅔ ozs. troy = 907.19 kilograms.

Metric Ton

1 metric ton = 1000 kilograms.

CONVERSION OF THERMOMETER READINGS

To convert Fahrenheit to Centigrade, subtract 32 and multiply by $\frac{5}{9}$.
To convert Centigrade to Fahrenheit, multiply by $\frac{9}{5}$ and add 32.

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